AST ENGINEERING
MAY 2 6 1948

JOURNAL OF

THE INSTITUTE OF PETROLEUM

FOUNDED 1913 INCORPORATED 1914

Vol. 34 APRIL 1948 No. 292

CONTENTS

	PAGE
The Structure and Properties of Ethylene Polymers. By R. B. Richards	237
Simple Chemical Analysis of *iso*Butene in Binary Mixtures with other Olefins. By J. P. W. Houtman	255
Lubricating Oil Testing in Engines. By R. Stansfield and J. C. Cree	271
Tank Calibration. By Tank Calibration Panel	288
Abstracts	87A
Applications for Membership or Transfer	i–iii

Published by the Institute of Petroleum.
Address: "Manson House," 26, Portland Place, London, W.1.
Telephone No.: LANgham 2250.
Telegraphic Address: Instpetech, Westdo, London.
Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk.

All rights of Publication or Translation are Reserved.
Price 7s. 6d. (Annual Subscription, £3 13s. 6d.) post free.

COUNCIL, 1947–1948

PRESIDENT :
Sir Andrew Agnew, C.B.E.

PAST-PRESIDENTS :

Alfred C. Adams
S. J. M. Auld, O.B.E., M.C., D.Sc.
J. S. S. Brame, C.B.E., F.R.I.C.
T. Dewhurst, A.R.C.S.
A. E. Dunstan, D.Sc., F.R.I.C.
F. H. Garner, O.B.E., Ph.D., F.R.I.C.
J. Kewley, M.A., F.R.I.C.

VICE-PRESIDENTS :

G. H. Coxon
E. A. Evans, M.I.Mech.E., F.R.I.C.
A. C. Hartley, C.B.E., F.C.G.I.
J. S. Jackson, B.Sc., F.R.I.C.
J. A. Oriel, C.B.E., M.C., M.A.
H. C. Tett, B.Sc., D.I.C.

MEMBERS OF COUNCIL :
H. C. Tett - Chairman

M. A. L. Banks, B.Sc., F.R.I.C.
A. T. Beazley, M.B.E., B.Sc., A.M.Inst.C.E.
E. J. Dunstan, M.Sc.
E. B. Evans, Ph.D., M.Sc., F.R.I.C.
F. L. Garton, M.A., B.Sc.
H. Hyams
V. C. Illing, M.A., F.R.S.
R. I. Lewis, B.Sc.
F. Morton, Ph.D., F.R.I.C.
J. S. Parker, M.A., B.Sc.
C. A. P. Southwell, M.C., B.Sc.
F. B. Thole, D.Sc., F.R.I.C.
A. Beeby Thompson, O.B.E.
G. H. Thornley, M.Sc.
E. Thornton, B.Sc., F.R.I.C.
R. R. Tweed
H. de Wilde, M.Sc., M.I.Mech.E.
W. J. Wilson, F.R.I.C., A.C.G.I.

EX-OFFICIO :

H. A. Ruffell, A. J. Featherstone } Northern Branch.
W. R. Guy, F.R.I.C. Scottish Branch.
R. B. Southall. South Wales Branch.
V. Biske, B.Sc., F.R.I.C., LL.B., H. E. F. Pracy, A.R.I.C. } Stanlow Branch.

HONORARY SECRETARY : C. Chilvers, B.Sc., F.R.I.C.
HONORARY TREASURER : G. H. Coxon

HONORARY EDITOR : F. H. Garner, O.B.E., Ph.D., F.R.I.C.
HONORARY ASSOCIATE EDITOR : E. B. Evans, Ph.D., M.Sc., F.R.I.C.
GENERAL SECRETARY : F. H. Coe
PUBLICATIONS SECRETARY : George Sell
TECHNICAL SECRETARY : Peter Kerr, M.A., B.Sc., F.R.I.C.
LIBRARIAN : Miss P. Knapp, A.L.A.

HON. SECRETARIES OF BRANCHES

Northern Branch: Mervyn Mason, Matthew Wells & Co., Ltd., Bolton Street, Manchester, 3.

Scottish Branch: W. Robert Guy, F.R.I.C., Scottish Oils Ltd., Middleton Hall, Uphall, Broxburn.

South Wales Branch: E. J. Horley, National Oil Refineries, Ltd., Llandarcy, Glam.

Stanlow Branch: J. G. Hancock, "Shell" Refining & Marketing Co., Ltd., Stanlow Refinery, Ellesmere Port, Cheshire.

Trinidad Branch: P. E. T. O'Connor, c/o Antilles Petroleum Co., Ltd., San Fernando, Trinidad, B.W.I.

Vol. 34. No. 292. April 1948.

THE INSTITUTE OF PETROLEUM.

An Ordinary General Meeting of the Institute of Petroleum was held at Manson House, 26 Portland Place, London, W.1, on Wednesday, January 14, 1948, Mr J. A. Oriel, C.B.E., M.C. (Vice-President), presiding.

The Minutes of the preceding Ordinary General Meeting, held on December 10, 1947, were read, confirmed, and signed.

The Secretary (Mr F. H. Coe) announced particulars of the next Ordinary General Meeting, to be held on February 11, and of a joint meeting of the Institute with the Institution of Chemical Engineers on February 23.

The following paper was then read by the author:

THE STRUCTURE AND PROPERTIES OF ETHYLENE POLYMERS.

By R. B. Richards.*

Ethylene Polymerization.

In view of the reactivity and unsaturated nature of ethylene it is not surprising that a great quantity of work has been devoted to attempts to polymerize it to materials of higher molecular weight. Egloff's book, *The Reactions of Pure Hydrocarbons*, devotes over fifty pages to the subject of ethylene polymerization,[1] and shows that a vast variety of different products have been obtained. The products of this early work were invariably relatively low molecular weight materials and were generally liquids or greases. Butenes, hexenes, and other olefins, as well as dienes and paraffins, were among the products. Catalysts included metals and metal halides, and the electric discharge was also used to initiate polymerization. High temperatures and pressures of the order of hundreds of atmospheres were used, but attempts to use higher pressures resulted in explosive decomposition of the ethylene to carbon and methane or hydrogen. In 1933 there was a great advance in the field of ethylene polymerization when it was found that at pressures of the order of 1000 atm and at temperatures around 200° C ethylene could be polymerized in the presence of a minute but carefully controlled amount of oxygen to yield solid polymers with molecular weights as high as 40,000.[2] In spite of the chemical engineering difficulties, including the tendency, noted above, of ethylene to decompose explosively to yield carbon, this process was developed on the commercial scale and the plastic material known as polythene has been extensively used since the beginning of the recent war as an insulating material particularly for radar cables and for submarine cables.

* Imperial Chemical Industries Ltd., Alkali Division.

It is believed that the mechanism of the polymerization of ethylene to high polymers is essentially similar to the mechanism of other vinyl polymerizations such as the production of polystyrene and polyvinyl chloride. It is thought that the reaction is initiated by free radicals. The function of the catalyst is to provide free radicals either by decomposition or by reaction with the ethylene. Peroxides, other peroxy compounds such as persulphates, and metal alkyls, are examples which form radicals by decomposition, while oxygen is believed to act by the oxidation of some of the ethylene to yield a free radical which initiates polymerization. The radical formed from the catalyst is believed to react with an ethylene molecule to form a larger radical which in turn adds a second ethylene molecule, and in this way builds up a polymer chain.

$$\text{Catalyst} \longrightarrow \text{free radical R—}$$

or $$\text{Catalyst} + C_2H_4 \longrightarrow \text{free radical R—}$$

$$\text{R—} + C_2H_4 \longrightarrow \text{R—}CH_2\text{—}CH_2\text{—}$$

$$\text{R—}CH_2\text{—}CH_2\text{—} + C_2H_4 \longrightarrow \text{R—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—} \text{ etc.}$$

This simple mechanism leads to a straight-chain polymer. Subsidiary processes such as the reaction of a growing radical with a previously formed polymer molecule may lead to branched chain products.

The degree of polymerization and the degree to which the molecule has a linear or a branched-chain structure can be controlled by variations in the polymerization conditions such as the pressure, the temperature, the catalyst concentration and the purity of the ethylene, and a wide variety of products can be produced.

The Range of Ethylene Polymers.

Ethylene polymers with molecular weight up to at least 50,000—that is, containing as many as 4000 linked carbon atoms—have been produced by high-pressure polymerization. The normal commercial polymers sold under the trade name of "Alkathene"[3] cover a molecular weight range from about 12,000 to 22,000. These are tough thermo-plastics intermediate in hardness and flexibility between rubber and rigid plastics such as polystyrene, and have a fairly sharply defined melting point at about 110° C. These, however, form only a part of a wide range of products which can be made by high pressure polymerization of ethylene. The complete range of experimental products includes plastics both harder and softer than the normal "Alkathenes," tough or brittle waxes ("Winnothenes"), soft waxes similar to microcrystalline waxes, pastes, greases similar to petrolatums and oils, and the liquid or gaseous products described in Egloff's book. The solid members of this range all melt at some sharply defined temperature to a liquid, or in the case of polymers of molecular weight, above about 25,000, to a rubber-like elastic material or to a gel.

The variations in the properties of ethylene polymers are to a great extent due to the variations in average molecular weight, *e.g.*, the products

of molecular weight below about 500 are oils or soft greases, products with molecular weight in the 1000 to 5000 range are stiff greases or waxes, products of molecular weight in the 8000 to 18,000 range are plastics which melt to a viscous liquid, and which become brittle on cooling to 0 to − 30° C, and products of molecular weight of 25,000 or above change to a rubbery condition on heating to 110 to 120° C, but remain flexible at temperatures as low as − 100° C to − 140° C.

The viscosity of the melt at some fixed temperature is intensely sensitive to molecular weight and indeed is used for the classification for the commercial ethylene polymers. Some idea of the variation with molecular weight of the viscosity at 120° C is given in the following table.

Molecular weight.*	Viscosity † at 120° C (poises).
114 (*n*-octane)	0·002
400 paraffin wax	0·025
1,000	0·1
2,500	1
4,000	10
7,000	100
11,000	1,000
16,000 "Alkathene"—Grades 2 to 200	10,000
22,000	100,000
29,000	1,000,000

* Calculated, for ethylene polymers, by Staudinger's solution viscosity method: the figures are not to be taken as absolute.

† The flow of high polymers is non-Newtonian and viscosity varies with rate of shear. The figures quoted are obtained under standard flow conditions.

It must not be thought, however, that average molecular weight alone governs the physical or mechanical properties of a polymer; samples of the same average molecular weight (all of them true ethylene polymers) may vary widely in properties. The variations are most marked at the lower end of the molecular weight scale. For example, of two ethylene polymers of average molecular weight 1000, the first may be a soft semi-fluid grease, melting to an oil at about 40° C, whereas the second may be a hard brittle wax with a sharp melting point of over 90° C. Of samples of higher average molecular weight, say, 20,000, one may have a melting point of 125° C and a Young's modulus of 4000 kg/cm², whereas the other melts at 110° and has a modulus of 1000 kg/cm². An indication of the cause of the difference in properties between these pairs of samples is given by measurement of their densities and by examination of their X-ray diffraction patterns. These show that the higher and harder melting samples have a more perfectly crystalline structure than the softer samples. In the course of work on the causes of the variations from sample to sample in the mechanical properties of polyethylene of a given average molecular weight, much attention has been paid to observations of the nature of crystallization in this type of polymer and to measurement of the perfection of crystallization.

Crystallization in Waxes and Polymers.

At ordinary temperatures ethylene polymers, except those of very low molecular weight, are white translucent solids which change at a well-defined temperature to a glass clear liquid or rubber. This change in transparency is associated with loss of all rigidity or tensile strength (except for the samples of highest molecular weight) and is, hence, akin to the melting of a crystalline solid. Microscopic examination of the high molecular weight polymers in the solid state shows some structure, but it is impossible to identify any feature of this structure with single crystals of the type found in ionic salts, low molecular weight organic compounds, or even waxes such as paraffin wax. No sharply defined planes, edges, or corners are to be seen. This has led people familiar with the low molecular weight crystalline or microcrystalline waxes to refer to the waxes or plastics made by the polymerization of ethylene as "colloidal" or even amorphous. Ethylene polymers are not, however, amorphous at ordinary temperatures; the X-ray diffraction pattern shows sharply defined spots or lines with spacings and indicate a crystal structure virtually identical with that of the pure *normal* paraffins such as hexatriacontane, with paraffin wax, or with Fischer–Tropsch waxes. The structure of polyethylene crystals has been worked out in detail.[4]

As a background to the sharp lines or spots on an X-ray powder photograph due to the crystals there is a more diffuse halo of the type characteristic of liquids or truly amorphous materials. This is not found in the perfectly crystalline low molecular weight *normal* paraffins. This diffuse halo indicates that there are regions of disorder or amorphous structure in the solid ethylene polymer. The relative intensities of the "crystalline" and "amorphous" lines varies from sample to sample and also varies with temperature, the amorphous band becoming more prominent as temperature rises.[5] At a temperature which is close to that at which mechanical strength is lost and at which the polymer becomes transparent the last trace of the sharp "crystalline lines" disappears.

Ethylene polymers, then, contain crystalline regions and amorphous regions, but the crystals are too small to be visible even under the microscope although they are, in details of the arrangement of the paraffin chains, almost identical with the crystals of pure *normal* paraffins. Even the electron microscope does not reveal individual crystals in high molecular weight polyethylene although, like the optical microscope, it reveals a definite structure in the solid state.[5] The crystalline regions in ethylene polymers as in other crystalline polymers such as cellulose, nylon, stretched rubber or gutta-percha are now believed to have dimensions of only a few tens of hundreds of Ångstrom units and to be composed of bundles not of whole molecules but of short lengths of molecules, so that one polymer molecule (which may be thousands of Ångstrom units long) may pass through a number of separate crystalline regions. Those portions of the polymer molecules which do not lie in parallel orientation in crystallites comprise the amorphous regions and give rise to the diffuse X-ray band.

The crystal structure of a high molecular weight ethylene polymer may be contrasted with that of a pure straight-chain paraffin; wax-like products with a distribution of molecular weight form an intermediate type

of structure. The pure normal paraffin crystallizes in many layers of slightly tilted molecules with the ends of the molecules coplanar (Fig. 1A). This regular structure extends in three dimensions to give individually, crystals big enough to be seen at least under a microscope. The single crystal may contain of the order of 10^{15} to 10^{20} and regularly arranged paraffin molecules. If the material is not homogeneous with respect to molecular weight a less perfect structure will result. On cooling from the melt the components of a mixture of paraffins may form separate solid phases, but a more general effect is the formation of solid solutions in which the components' different chain lengths lie side by side. This necessarily makes the planes formed by the ends of molecules less well-defined and the general perfection of crystallization is reduced.

As molecular weight increases the viscosity of the melt rises and the readiness with which the molecules can flow to a growing crystal, straighten out from the coiled state characteristic of the melt and align themselves in a crystal is reduced. We find therefore that the number of molecules in a crystal tends to decrease as molecular weight rises, so that when the molecular weight is above one or two thousand, individual crystals can no longer be seen.

An interesting phenomenon which is allied to the effect of increased molecular weight on the size of crystals in paraffin is that the addition of a relatively small amount of an ethylene polymer to paraffin wax causes a great reduction in the size of the individual crystals. For example, 1 per cent of "Alkathene" may reduce the average volume of crystals formed by cooling paraffin wax from the melt by as much as one-thousand fold. This reduction in crystal size is associated with an increase in hardness and toughness and by an increase in density, indicating a more compact structure.

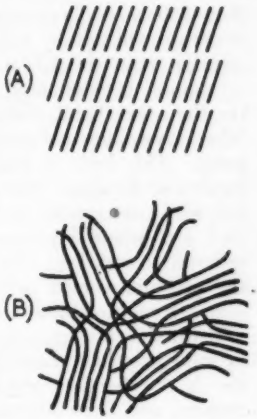


FIG. 1.

SOLID STRUCTURES OF LOW AND OF HIGH MOLECULAR WEIGHT PARAFFINS.

(A) CRYSTAL STRUCTURE OF A PURE PARAFFIN, E.G., $C_{32}H_{66}$.

(B) SOLID STRUCTURE OF A HIGH MOLECULAR WEIGHT ETHYLENE POLYMER.

In the case of a true high polymer, when the molecules in the very viscous melt form a tangled mass, crystallization will start at scattered points (perhaps where there are local parallel alignments of sections of molecules) and each nucleus will be composed of segments of a different selection of molecules. As cooling proceeds, greater and greater lengths of molecules will take their place in crystallites, but unless a break-up and re-formation of crystals occurs it will be impossible for every portion of each molecule to find a place in a crystal. The lengths which do not find a place in the crystalline regions form the amorphous regions of the polymer (Fig. 1B).

In the case of a polyethylene of molecular weight in the region of 10 to 20,000 it is believed, on the basis of X-ray examination and on other

grounds, that on the average about 100 molecules lie in a crystal and that the segment of a molecule which lies in a good crystal contains about fifty carbon atoms. Thus an average molecule containing, say, 1000 carbon atoms may pass through ten to twenty separate crystallites. Some polymers such as cellulose or rubber are believed to form bigger crystallites than these. In others, such as unplasticized polyvinylchloride, the regions of order are so small and ill-defined that polymer chemists are not agreed as to whether it should be called crystalline or amorphous.

It will be noted that the linear dimensions of the crystallites quoted above for polythene are less than the wavelength of visible light although the density and hence refractive index of the crystalline is different from that of the amorphous regions. Such a partly crystalline, partly amorphous structure will not by itself scatter light if the crystallites were randomly oriented and, indeed, it is possible to have a polymer which, though crystalline, is glass clear: cellulose and cellulose derivatives are examples. On the other hand, the most familiar form of polythene, and of many other crystalline polymers, is translucent or opaque below the melting point. This lack of transparency is due to the scattering of light by structural features which are much larger than the individual crystals and which are readily seen under the microscope. The units of this structure are oriented groups of crystallites. In one form, known as the spherulitic structure, the crystallites are arranged around a nucleus with the polymer chains perpendicular to the radius. Under crossed nicols such a structure shows up as a dark maltese cross on a light ground.

Estimates of the proportions of amorphous and crystalline material in solid polythene have been made by a comparison of the intensities of the X-ray bands corresponding to the amorphous and the crystalline regions, and from measurements of the density,[6] the heat content,[7] and the heat of solution[7] of ethylene polymers. At temperatures below about 60°, the proportion of crystalline material in an average sample of "Alkathene" remains steady at about 70 per cent. Wide variations in the crystalline content of experimental samples of ethylene polymers made under different polymerization conditions are observed, however, even among samples of the same average molecular weight. A range of from below 50 per cent to above 90 per cent in the proportion of crystalline material has been observed for samples of molecular weight above 1000. These changes in crystallinity lead to the variations in the mechanical properties of the solid mentioned above. Examples of properties which are sensitive to the proportion of crystalline material are:—

Surface hardness;
Young's Modulus, or stiffness;
Softening point by an indentation or penetration test;
Yield point (*i.e.*, the stress in tension at which the sample breaks, if of low molecular weight, or changes into a highly oriented form by the process known as "cold drawing," if the molecular weight is high) (Fig. 2);
Swelling by oils or other organic liquids.

The properties listed above are relatively insensitive to average molecular weight, except inasmuch as this affects the degree of crystallinity.

(There is a tendency, among a series of samples of similar chemical structure but different chain length, for the lower molecular weight samples to be slightly more crystalline.) It should not, however, be thought that all mechanical properties are insensitive to chain length. The tensile strength of an oriented fibre is primarily governed by average molecular weight. Toughness, impact strength, flex resistance, and tear resistance are other properties which are governed mainly by average molecular weight. Generally speaking, the properties which only concern minor movements of elements of the solid structure relative to each other are affected most by degree of crystallinity. If, on the other hand, rupture or considerable deformation of the solid occurs, the length of the constituent molecules is

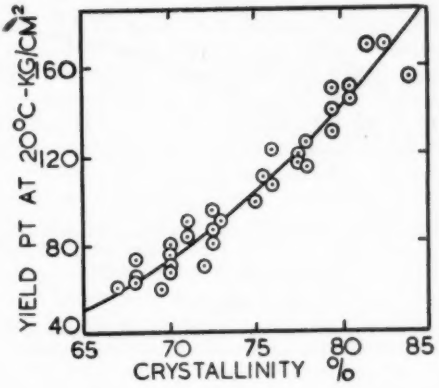


FIG. 2.

EFFECT OF CRYSTALLINITY ON YIELD POINT IN TENSION.

more important. Flexibility at low temperatures is particularly sensitive to molecular weight, and when the molecular weight increases from about 20,000 to about 25,000, there is a sudden change in brittleness temperature from about — 30° C to below — 140° C.

The general effect of crystallinity and of molecular weight on the physical properties of ethylene polymers is shown in Fig. 3. The shaded area represents the range of experimental products which can be made by variation of polymerization conditions and the position of the more familiar types—" alkathenes " and " winnothenes " (polyethylene waxes)—is indicated.

The optimum chain length and degree of crystallinity of a polyethylene sample depends on the use for which it is destined, and both the properties of the final product and the mode of fabrication must be considered. Frequently there must be a compromise. For example, for cable insulation the product should not be too crystalline, or the cable will not have sufficient flexibility, and the molecular weight should be as high as is possible (to give increased toughness), but a limit is set by considerations of extrusion rate. For mouldings a higher molecular weight or viscosity is tolerable, while for fabrication techniques assisting flow casting, or spreading (as,

for example, for waterproofing paper) a low viscosity product is required. For the latter use also the product should be flexible—that is, the crystallinity should be low. For hardening of paraffin wax or in the allied use as a component of polishes a high degree of crystallinity is required, and here a low molecular weight is desirable as it increases the rate of solution in the wax or solvent.

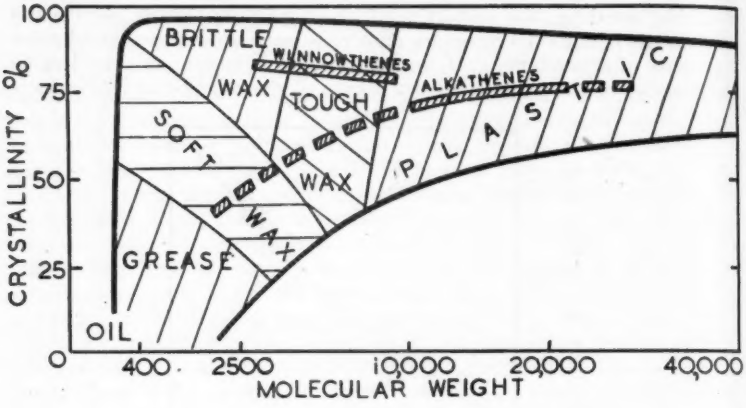


FIG. 3.

RELATION BETWEEN CRYSTALLINITY, AVERAGE MOLECULAR WEIGHT, AND THE PHYSICAL PROPERTIES OF ETHYLENE POLYMERS.

CRYSTALLIZATION AND CHEMICAL STRUCTURE.

The extent to which the molecules in a sample of ethylene polymer can take their places in crystals is governed mainly by the detailed chemical structure of the polymer. Average molecular weight and breadth of distribution of molecular weight about the average are of some importance, but the main feature is the extent to which the molecule is an unbranched chain of methylene groups. The effect of constituent groups other than methylene caused by interpolymerization of ethylene with other monomers or by chemical treatment of polyethylene is discussed later. In polymers and ethylene alone, the main cause of variation in crystallinity is the presence of branched-chain molecules. Short side chains, such as methyl or ethyl groups, cannot fit into the normal crystal structure, nor can the atoms in the region of a fork in a molecule which carries long side chains, although part of the branches may themselves lie in crystals.

Infra-red analysis [8] is one of the most powerful tools for the determination of the degree of branching in ethylene polymers. The indications are that the degree of chain branching may be as high as one side chain for every twenty methylene units, although ethylene polymers, in which chain branching can hardly be detected, can be made. These products are similar to the high molecular weight Fischer–Tropsch waxes made from carbon monoxide and hydrogen over a ruthenium catalyst.[9] These are believed to be entirely unbranched polymethylenes and are very highly crystalline.

If high molecular weight polyethylene is mixed with a pure low molecular weight paraffin, or with paraffin wax, both of which are almost completely crystalline, the resulting product is, as might be expected, rather more crystalline than the original polythene. It was noted above that certain properties, notably surface hardness, stiffness, and yield point in tension, are governed by crystallinity rather than by molecular weight. Hence, despite the reduction in average molecular weight by the addition of the wax, the blend is somewhat harder and stiffer, and has a higher yield point than the unmodified polymer. It is a rather unexpected result to find that an increase in hardness is caused both by the addition of a little polythene to paraffin wax, and by the addition of a little paraffin wax to polythene.

So far we have only considered polymers of pure ethylene. By incorporation of other monomers of the vinyl type in the reaction system, interpolymers may be made.[10] The general effect of the second component on the mechanical properties of ethylene polymer is a reduction in softening point and hardness. This is a consequence of the inability of the sections of the molecules incorporating the second component to crystallize in the polymer structure. Examples are the interpolymers with small quantities of isobutene, methyl methacrylate, styrene, and vinyl acetate, all of which have lower softening points than polymers of ethylene alone.

A similar effect is observed if the polyethylene structure is modified by chemical reaction. A good example is chlorination,[11] in which hydrogen atoms are replaced by chlorine atoms. Here the chlorine atoms are too large to fit into the polyethylene crystals and hence, as the chlorine content increases, the softening point falls, so that a product containing 40 per cent of chlorine is a soft, rubbery material. A parallel effect at a lower molecular weight is the production of a liquid by the chlorination of paraffin wax.

If the proportion of the second component in an interpolymer becomes large, there may be a rise in softening point after the initial fall. This will be the case where the pure polymer of the second monomer has itself a high softening point. Examples are the interpolymers with methyl methacrylate or styrene. A similar rise in softening point after an initial fall is shown in the case of chlorinated polythenes of high chlorine content. The high softening point and hardness in these cases is due not to crystallization, but to modification of the flexibility of the molecules in the amorphous state.

Although interpolymerization and substitution lead to a less regular molecular structure, and generally cut down degree of crystallinity, they do not necessarily have this effect; for example, ethylene can be interpolymerized with carbon monoxide to form a polyketone

$$-(CH_2-CH_2)_n-CO-(CH_2-CH_2)_m-CO-$$

and an interesting feature of this class of interpolymer is that the melting point and hardness are only slightly affected by the proportion of carbonyl in the sample. It has recently been shown that the reason for this is that the carbonyl group is similar in size to the methylene group, and can fit into the crystals with only slight distortion of the crystal lattice. Other chemical groups can be accommodated in the polyethylene crystals [12]

with only minor distortion, the phenomenon being akin to isomorphous replacement in ionic crystals such as of iron and aluminium in the alums. Such mixed crystal formation in polymers may, however, be regarded as the exception rather than the rule, and in general it is fair to say that an irregular structure tends to reduce crystallinity.

References.

[1] Egloff. *The Reactions of Pure Hydrocarbons.*
[2] B.P. 471,590.
[3] See, for example, *British Plastics*, March, April, and May, 1945.
[4] Bunn. *Trans. Faraday Soc.*, 1939, **35**, 482.
[5] Bunn and Alcock. *Trans. Faraday Soc.*, 1945, **41**, 317.
[6] Hunter and Oakes. *Trans. Faraday Soc.*, 1945, **41**, 49.
[7] Raine, Richards, and Ryder. *Trans. Faraday Soc.*, 1945, **41**, 57.
[8] *E.g.*, Thompson and Torkington. *Trans. Faraday Soc.*, 1945, **41**, 246.
[9] Pichler and Buffleb. *Brenn. Chem.*, 1940, **21**, 257.
[10] B.P. 497,643.
[11] B.P. 481,515.
[12] Bunn and Peiser. *Nature*, 1947, **159**, 161.

Imperial Chemical Industries Research Department,
Alkali Division,
Northwich.

Discussion.

The Chairman (Mr J. A. Oriel): I am sure we are very much obliged to Dr Richards for the very lucid way in which he has presented his paper. It is true, as he has said, that some years ago it would have seemed very strange to some of us that this Institute should meet to discuss the polymers of ethylene; ethylene itself was merely something which was burned with so much else. But as time has gone on, although we are still essentially an industry dealing with fuels and lubricants, we are slowly being drawn into the chemical industry and we are taking a greater and greater interest in the type of work which Dr Richards has discussed. The availability of ethylene from the petroleum industry, I imagine, is greater than from any other source, and eventually I think the petroleum industry will be the cheapest source of ethylene. I think also that, as Dr Richards has pointed out, we shall need high pressure technique in order to carry out this polymerization, and here, too, the petroleum industry has much to offer.

Dr Richards has devoted his talk chiefly to a consideration of the relationships between the physical and chemical properties of the polymers and their performance, and if I were to ask questions in that field I should merely reveal my abysmal ignorance. But I know there are many present who would like to ask detailed questions, and he has expressed his willingness to answer all the questions in connexion with the polymerization of ethylene, whether or not the questions concern matters he has touched on in the paper.

Mr A. V. Billingham: A point which emerges quite clearly from this paper is that we must no longer think just of polythene or alkathene, *i.e.*, of just a particular kind of plastic. We are all familiar with the better known type, with its outstanding properties in the electrical field. But Dr. Richards has pointed out that we have in the polyethylenes a whole

range of plastics having various properties, leading to all kinds of possible uses, again bringing the ethylene-producing industries possibly, and I think probably, closer and closer to the large consuming industries in the world. The paper is interesting not only to pure scientists and chemists, and to the chemical engineer concerned with high pressure reactions, but also to the petroleum technologist.

A point I have in mind, and which is brought out when one reads the paper, is the variation that can occur in crystallinity and molecular weight. I notice one reference to a synthetic fibre, and I think we all realize that in this world, emerging as it is to-day, there will be a very big demand for fibres. We have seen the development of quite a lot of synthetic fibres, such as the modified cellulose fibres, and so on. I should be glad if Dr Richards could give us some lead or some information on the possibilities of polyethylene or ethylene polymers in that field. For example, I think we all have to recognize that fully synthetic fibres possess both advantages and limitations. One may anticipate that polythene fibres may be used in spinning, in carding, and so on, and hence electrostatic properties are important. The question of solubility in hydrocarbon arises in connexion with the possibility of dry cleaning.

In the fibre one introduced an exaggerated effect; the surface–volume ratio in that physical form is very much higher than it is in other forms, and therefore, any susceptibility to deterioration of properties, as, for example, on exposure to ultra-violet light, is important.

Another important property would be water absorption; low water absorption is undoubtedly very important. Can Dr Richards suggest how important that is in synthetic fibres, because when clothing is made of such fibres we have to consider the absorption of moisture from perspiration, and the hygienic and health aspects which are involved?

Coming to a rather different field, that of considering the polymers rather as chemical intermediates, I would like to know whether any work has been done on, or whether there are indications of the value of, the ketones as chemical intermediates, possibly as surface-active compounds, and so on?

MR RICHARDS: First there is the question of producing fibres from polythene. As a general-purpose fibre which would, for instance, replace silk or nylon, it does not seem to me personally that polythene will ever be satisfactory. I do not think Mr Billinghame mentioned the main difficulty, which is its melting point of about 110° C. That is just too low for general use in clothing, for the fabric would melt at the temperature normally used for ironing. But for specialized purposes, and particularly where resistance to the effects of water and to chemical attack is required, there does seem to be a potential use for polythene in fibre formation. As an example, in a recent American plastics journal I saw a photograph of a polythene clothes line, and there have been advertisements of chair seats and backs made from woven polythene fibres. Polythene filaments have been used as surgical sutures.

There are many other specialized uses where resistance to water or to chemical attack is important and where polymers of ethylene are likely to become useful.

The question of deterioration and the high surface–volume ratio is important, of course. Although polythene is not entirely resistant to the action of sunlight its substantially saturated paraffinic structure renders it one of the most stable of polymers to weathering.

I imagine that, in the case of a fibre to be used for textiles, the water absorption is a very important property. Certainly a large number of papers have recently been published on the water-absorption isotherms of such materials as wool, hair, silk, and nylon. In the case of polythene the water absorption is very low, of the order of only 0·1 per cent at 75 per cent relative humidity.

With regard to the uses of the ketones formed from ethylene and carbon monoxide, the study of this subject is in the very early stages at the moment. The question as to whether one can produce commercially useful materials by making a polyketone and further treating it is as much a matter of economics as of organic chemistry; the subject is under active investigation.

MR D. A. C. DEWDNEY: On the question of economics, I have the impression that the ethylene required for the production of polythene must be essentially 100 per cent pure. I should imagine that the presence of ethane and methane may not be deleterious, except that you have to compensate for dilution of the ethylene by raising the total pressure. But the production of extremely pure ethylene is very expensive as compared with making a concentrated C_2 cut.

MR RICHARDS: That is perfectly true. The quality of ethylene required for the controlled manufacture of polythene has to be very high indeed; it has to be substantially 100 per cent, and it has to be constant at 100 per cent, which is perhaps even more important. Some materials are very much more deleterious than others. I would not like to say that we know the effect of all the materials which are potentially present in ethylene from petroleum, but there are very few impurities which have not a very marked effect on the polymerization of ethylene, the most serious effect being the changing of molecular weight.

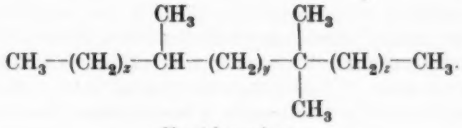
DR C. M. CAWLEY: I particularly appreciate Mr Richards' account of the conception of partial crystallization and its relation to the plastic properties of polythene.

One point he had not fully grasped is the extent and nature of the branching which occurs in ethylene polymers. Mr Richards has said that Fischer–Tropsch waxes are practically unbranched polymethylenes and this is certainly true of the high-molecular-weight waxes obtained by the use of a ruthenium catalyst. The low-molecular-weight waxes obtained by the Fischer–Tropsch process as operated commercially in Germany did, however, contain some branched-chain material, perhaps as much as 20 per cent, although the waxes were still less branched than petroleum waxes of comparable molecular weight. I understand that the extent of branching in ethylene polymers decreases with increase in molecular weight, but I should like to know whether the branching, for any particular molecular-weight range, is uniform in nature and extent; for example, are the branches simple methyl groups uniformly distributed, or are they more complex side chains heterogeneously distributed?

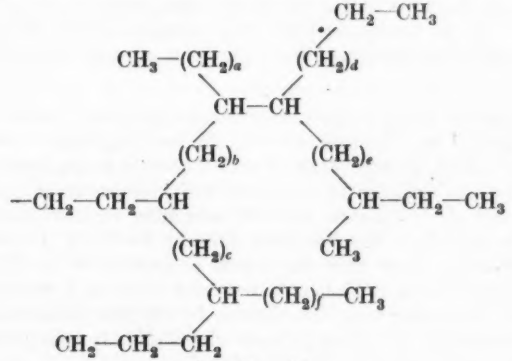
MR RICHARDS: In a normal sample of polythene of the type used for electrical purposes we think that there is on the average one branch for, say, every fifty carbon atoms along the main chain. That means that in a product such as "Alkathene" 20 with about 1000 carbon atoms on the average molecule, there will be about twenty branches per molecule. I feel sure that the branching is fairly evenly distributed from molecule to molecule. That is an average electrical-grade polythene. If it were not for the branching in this type of material it would not be of any use for insulation; it would probably be brittle at low temperatures, and it would not have sufficient flexibility for use as a cable insulation.

In the special experimental samples I think the degree of branching can be reduced to the order of one branch for every 200 methylene units along the chain, and it can be increased to as much as one in every ten. I think the grease which I have exhibited here is very highly branched, there being one branch for about every ten carbon atoms along the chain.

As to the type of branching, there are two main types which arise in slightly different ways in polymerization. One of them is just a methyl side group. That is the type of product obtained by interpolymerizing ethylene with propylene or butylene. Such a side group cannot fit into the crystal structure at all. There is another type of branching, we think, in which there are long side chains. These branches are so long that they can take their place in crystalline regions, with the exception of the atoms in the region of the tertiary carbon atom. Such a network structure shows itself by other properties, particularly the viscous flow of the molten polymer:



Short branches.



Long branches.

MR V. BISKE: Mr Richards has said that one of the main advantages of the polyethylenes is in connexion with their electrical properties including,

I presume, a low power factor. Can he say whether those properties vary in a particular way with molecular weight, or vary according to whether the material is crystalline or amorphous?

MR RICHARDS : Very little. In the case of molecular weight, I should say not at all over the range with which we are normally concerned. About crystallinity, one would expect a small effect. I think the electrical properties depend on the number of dipoles and the dipole moment and on the environment in which the dipoles can rotate or move under the influence of an electrical field. The carbonyl dipole in the ethylene–carbon monoxide interpolymer is a good example, for the carbonyl group can lie either in a crystalline or in an amorphous region; the resistance to rotation in the electrical field in the crystalline region will be different from the rotation in the amorphous region. If you vary the amount of crystalline material you would expect a variation in the power factor. It has recently been shown by Jackson and Forsyth in the *Journal of the Institution of Electrical Engineers* that the power factor of polythene can be partly attributed to carbonyl groups formed from traces of carbon monoxide in the ethylene, and one would therefore expect a similar effect of crystallinity on the power factor.

MR E. THORNTON : Is there a theoretical explanation of the remarkable fact that you get variation of molecular weight from something very small to hundreds of thousands with no change of melting point?

MR RICHARDS : I think that the most satisfactory explanation is that the small crystallites in the polymer solid (Fig. 1B) melt independently of each other; the melting point is dependent more on the size of the individual crystallites than on the number of crystallites through which a molecule of average length passes. The asymptotic approach to a constant melting point as molecular weight increases in a homologous series is, of course, a well-known phenomenon.

MR D. L. C. JACKSON : How do the chlorine atoms occur in chlorinated polythene? In particular, is there any indication that the presence of chlorine atoms in the molecule affects the point of entry of further chlorine atoms?

MR RICHARDS : There is some evidence on that point, based on infra-red work by Dr H. W. Thompson. Chlorinated polythene contains both $>CHCl$ and $>CCl_2$ groups, each of which gives a characteristic infra-red band. It is also possible to calculate the proportion of each of these groups at any given chlorine content, assuming random substitution of hydrogen by chlorine; this has been done by Mr W. F. L. Dick. Infra-red measurements show that the actual proportion of $>CCl_2$ groups in chlorinated polythenes is higher than would occur as a result of random substitution, indicating that substitution by chlorine atoms tends to take place preferentially on carbon atoms which already carry one chlorine atom.

DR A. WOLF : Like the chairman, but probably with much greater justification, I also confess to abysmal ignorance of polymer chemistry at

least in so far as solid polymers are concerned. However, I should like to ask Dr Richards, first, can he tell us from what particular source it is best to obtain the ethylene? Is there, for example, any advantage in using the ethylene obtained from coke-oven gas, *i.e.*, can it from this source be readily obtained sufficiently pure as a raw material for polymer manufacture, or is it preferable to obtain ethylene from some other source, such as the permanent gas formed during the production of cracked gasolines?

Secondly, what are the chief applications of these polythenes in the electrical industry, what substances previously in use do they replace, and what great advantages do they offer over the latter?

Thirdly, there was some reference by a previous speaker to the presence of static electricity on the surface of articles made of polythene. Is that a great drawback in any of the industrial applications of these polythenes, and if so, is there any method whereby it can be avoided? There are many instances, such as in the manufacture of certain synthetic fibres and plastics where I think static can give quite a lot of trouble.

Lastly, there was some mention of oxidation. I think that is quite likely to occur, for instance, where polythene is being melted in contact with air as a preliminary to its extrusion. I imagine the material must be heated to some degrees above its melting point. Is oxidation under those conditions rapid, is it of a nature similar to the oxidation of many petroleum products, particularly paraffin waxes, which chemically polythenes so closely resemble, what types of oxidation products are formed, how can the oxidation be minimized, and do those oxidation products affect the electrical and other properties adversely?

Mr Richards: I do not really feel competent to answer the question concerning the sources of ethylene; I feel there are others present here who can answer it far better than I can. However, it must be essentially 100 per cent ethylene; in particular it must be free from carbon monoxide, which causes the unwanted electrical properties which formerly turned up occasionally. The question of the source of ethylene to use is entirely a matter of which source will give us the cheapest ethylene of the required degree of purity.

In the electrical industry the material which I think polythene most obviously displaces, or partially displaces, is gutta-percha, which is in many ways very similar to polythene. It is softer and it has a lower melting point, melting at about 60° C instead of 110° C, but it has a partially crystalline, partially amorphous, structure similar to that of polythene. Polythene replaces it on the grounds of better electrical properties; it has a lower conductivity, lower permittivity, and lower power factor. It also has a better resistance to water, and the higher melting point is also an advantage. Gutta-percha was used primarily for submarine cables, and it is there that polythene is replacing it. The main use for polythene during the recent war was as a high-frequency dielectric in radar equipment. Radar and polythene were developed concurrently, and it is difficult to say what would have been used for high-frequency insulation if polythene had not been available.

One of the good features of polythene as an electrical insulator, the high surface resistivity, is the cause of the defect mentioned by Dr Wolf, the

development of static charges and the resultant tendency of polythene to pick up dust. This would be a serious matter, especially in the case of decorative articles, such as lampshades, made from polythene sheet, but it has been found possible to prevent it by additions to the polythene.

The prevention of oxidation is relatively simple. There are many anti-oxidants for polythene, and the incorporation of quite a small quantity (*e.g.*, 0·1 per cent) of one of them inhibits completely the oxidation of polythene at the temperature required for processing. I see that Dr Goldstein is here, and he probably knows more about the behaviour of anti-oxidants than I do; I remember discussing the choice of an anti-oxidant for polythene with him some years ago. The quantity of anti-oxidant that you have to put into polythene is very much less than the quantity you have to put into rubber, possibly because rubber is an unsaturated material and is hence more prone to oxidation than the substantially paraffinic ethylene polymers.

The subject of the products of oxidation is one to which a whole lecture might be devoted; but I can summarize roughly. The oxidation by atmospheric air is serious, in the absence of anti-oxidants, at temperatures of about 120° C and upwards. It is particularly awkward because the action is auto-catalytic, so that during the processing of unprotected polythene on mills or in an internal mixer each succeeding batch becomes worse and worse due to contamination with the residues of partly oxidized polythene from the previous batch.

The main chemical effects are the introduction of carbonyl groups, and in a later stage of oxidation hydroxyl and carboxyl groups are also formed. The molecular weight of the polymer may be decreased or cross-linking, with consequent increase of molecular weight, may occur. My own personal view is that the first product of oxidation is a hydroperoxide group, which later reacts to give carbonyl and so on.

The main physical effects are a deterioration in electrical properties, notably a rise in power factor at high frequencies due to the introduction of polar groups, and a change in viscosity and in flow behaviour. The cross-linking mentioned above leads to poor extrusion behaviour. Oxidation also causes discoloration, and prolonged oxidation yields a dark brown, brittle solid. The use of anti-oxidants has, however, put an end to these troubles.

MR E. A. EVANS: The only polymers mentioned this evening which are used in lubrication are the poly*iso*butenes. There was a great desire to use that kind of polymer before and during the war, but it was difficult to dissolve them in oil. How does one get them into solution?

Polymers would be popular if they were not so subject to high rates of shear. We are told that they break down very quickly. Is that true, and if it is true, are there any means of overcoming the difficulty?

The author has said that when these materials melt they become oil-like substances. Does that mean that they vary in viscosity as do oils, that there are some which are very thin and others which are thick?

These things are of tremendous interest to those concerned with the field of lubrication, and I am wondering whether some of these outstanding ideas are true.

MR RICHARDS: It is very difficult to get poly*iso*butene into solution quickly. I have not worked on that matter very much, but my own experience is that you have just to wait; you can continue stirring and kneading, and it goes into solution very slowly. I cannot help you at all with regard to evolving a quick method. On the laboratory scale one just puts the material into the solvent and leaves it there all night.

It is well known that high shearing forces on polymers do cause degradation. Work has been done on the calculation of the amount of energy which can be put into the individual molecules by mechanical shear, and it is quite sufficient to cause degradation. You are suggesting that for lubricant additives shear is high enough?

MR EVANS: Yes.

MR RICHARDS: I was not aware of that. I cannot say that I am surprised, but I cannot make any suggestion as to how to get away with it. It seems that the rate of degradation is a straightforward function of the energy applied in the form of shear. The effect is most marked with the higher-molecular-weight polymers, I believe, and there is a sort of lower limit of molecular weight below which degradation does not occur.

The viscosity of ethylene polymers in the molten state is intensely sensitive to molecular weight. I have given a table in the paper; a very slight change in molecular weight will cause a very big change in viscosity, a change from a light oil to a heavy oil. I have exhibited a grease which, when heated to about 70° C, melts to an oil which is similar to medicinal paraffin in consistency, and the viscosity varies with temperature in a manner very similar to that of ordinary hydrocarbon oils.

MR A. V. BILLINGHAME: In fabrication I understand that welding is something of a problem, which rather puts a premium on the development of completely satisfactory adhesives. What are the prospects of obtaining really adequate adhesives which will overcome the difficulties?

With regard to water absorption, obviously the polymers would appear to have quite big potentialities for thin film or foil. I wonder if Dr Richards could say the limits of film thickness to which it is possible to get down to by calendering or stretching or something of that kind.

MR RICHARDS: I know of no general-purpose adhesive for polythene. On the other hand, I think Dr Billinghame has given an unnecessarily gloomy impression of the difficulties of welding. The technique of welding polythene has made great strides, and many articles are now fabricated from polythene sheet by this method; you will see descriptions of the process in some of the Plastics journals. The main thing, I believe, is to use a polymer of suitable molecular weight, so that it neither flows away from the joints nor remains as a rubbery mass which does not stick to its neighbour.

I think that very soon now you will see polythene film a few thousandths of an inch thick in Britain. It is already used in America for wrapping food, cigarettes, and so on, and I believe the Americans have even made mackintoshes with it. It is a very good packaging material; it has a good resistance to water vapour, and its flexibility and elasticity is an advantage when articles with sharp edges are to be wrapped.

Vote of Thanks.

The Chairman : We should all like to join in thanking Mr Richards for having given us a most interesting evening. To me it has been quite a revelation; the paper and discussion have helped a large number of us, who had looked at this subject from the fringe, to get well into the middle of it. You will agree that Mr Richards has cheerfully and very lucidly answered all the questions put to him. On behalf of the Institute I should like to thank you very much, Mr Richards, not only for your lecture, but for the way in which you have answered the questions raised.

(The vote of thanks was carried with acclamation.)

SIMPLE CHEMICAL ANALYSIS OF *iso*BUTENE IN BINARY MIXTURES WITH OTHER OLEFINS.

By J. P. W. Houtman.*

Summary.

A simple method of analysis was developed for binary mixtures of *iso*-butene with propene, butene-1, butene-2, *iso*butane, and butadiene, using aqueous hydrochloric acid at room temperature as a reagent and the Bunte method of gas analysis. Only *iso*butene reacts with formation of *tert.* butyl chloride. The other gases possess, however, a fairly considerable solubility in the reagent, for which it is necessary to apply a correction. Undiluted mixtures can be analysed with an accuracy of approximately 1 per cent, when containing less than 85 per cent of *iso*butene. Above this value it is advantageous to dilute the gas with an equal amount of indifferent gas, such as air, in which case the same accuracy will be reached. Only mixtures with butadiene show a different behaviour when using the latter method.

Introduction.

It is a well-known fact that the reactivity of olefins in several addition reactions is connected with their structure. The behaviour of compounds having an unsaturated tertiary carbon atom is particularly striking as these compounds react many times faster than compounds without this special configuration.[1] It is this property that is used in all quantitative methods of analysis of these tertiary olefins in mixtures with others and especially in the determination of *iso*butene in cracking gases.

In most cases the reaction with sulphuric acid was used,[2] and in a single case the reaction with hydrochloric acid [3] or other reagents, such as a modified Denigès reagent.[4]

As all these methods require a more or less intricate apparatus, a method using only simple instruments is of interest. This applies even after the development of modern methods of analysis such as those employing the mass spectrometer [5] or infra-red spectrometer,[6] particularly when cost has to be considered.

In the thesis of Keulemans [7] some references were found to a simple method of analysing *iso*butene in mixtures with other isomeric butenes and butanes carried out in a normal Bunte burette, using an aqueous hydrochloric acid solution as a reagent.

It was learned verbally from Dr Visser that his method had been developed primarily for the rapid analysis of technical C_4-fractions of cracking gases. For this restricted purpose (gases with total olefin content not over 50 per cent, *iso*butene content not over 25 per cent) the method gave results of sufficient accuracy if a constant empirical correction of + 0·4 ml was applied to the final reading in the burette. Dr Visser, however, did not feel certain about the possibility of applying his method to mixtures of olefins only, as the corrections for solubility of gases in the reagent and the vapour pressure of the *tert*-butyl chloride

* Laboratory, N.V. de Bataafsche Petroleum Maatschappij, Amsterdam.

formed might then be quite different. As, on the other hand, the method is very simple and rapid, Dr Visser definitely encouraged the author in his project to investigate this matter more thoroughly.

The results of this investigation are communicated in the present paper. The determination of *iso*butene in gas mixtures containing not only isomeric olefins but also saturated hydrocarbons was not specially investigated, so that application of the present data to cracking gases is not permitted.

Preparation of Materials.

In agreement with the statement of Visser, an aqueous hydrochloric acid solution prepared by dilution of concentrated hydrochloric acid solution ($d = 1{\cdot}19$) with an equal volume of water and saturated with NaCl was used as the reagent.

Several gaseous olefins, a single diolefin, and one paraffinic hydrocarbon gas were investigated as the second component in binary mixtures with *iso*butene.

iso*Butene*.

The *iso*butene was prepared by boiling *tert*-butyl alcohol with anhydrous oxalic acid in a round-bottomed flask provided with a reflux condenser.[8] The *tert*-butyl alcohol was provided by Shell Chemical Co (U.S.A.) and was of high purity. The only impurity proved to be water. Addition of a small amount of sodium wire, followed by distillation of the remaining alcohol resulted in a product with a freezing point of 25·40° C (lit. : 25·55;[9] 25·4 [10]).

The crude *iso*butene contained only a small amount of alcohol, carried along with the *iso*butene vapours, and proved to be free of normal butenes. A portion of the product was hydrogenated in an autoclave with hydrogen under pressure and nickel on diatomaceous earth as a catalyst at a maximum temperature of 150° C. The resulting product was sharply distilled in a Podbielniak column packed with copper spirals. The whole sample boiled at a constant temperature corresponding with the boiling point of *iso*butane.* The crude *iso*butene was further separated from the alcohol by sharp fractionation in the Podbielniak column.

Propene.

The propene was prepared by dehydration of *iso*propyl alcohol (100 ml) by a mixture of concentrated sulphuric acid (75 ml) and aluminium sulphate (10 g) by boiling in a round-bottomed flask with a reflux condenser.[11] The yield was only 36 per cent and the reaction product contained SO_2, which was removed by repeated washing with an aqueous solution of NaOH.

Butene-1.

The butene-1 was prepared by decomposition of butanol-1-acetate by passing it over glass wool at *ca* 500° C. Both the alcohol, which was used as the starting material for the preparation of the acetate, and the acetate

* With this method an impurity of 0·2 per cent of *n*-butane will be found.

itself were purified by fractionation in an externally-heated, 2-m high, all glass distillation column (eighteen theoretical plates*).

The crude butene-1, freed from acetic-acid vapours by washing with NaOH solution, was carefully distilled in the Podbielniak column, during which process it proved to contain small amounts of butene-2.[12] The present investigations were carried out using a middle fraction with constant boiling point which can certainly be considered to be reasonably pure.

Butene-2.

The butene-2 was separated from a mixture of butenes which was formed by dehydration of *iso*butyl alcohol by passing it over aluminium oxide at 400° C. During this reaction a certain amount of isomeric butenes is always formed. In this case two different samples of Al_2O_3 were used as a catalyst, the first being α-Al_2O_3 formed by heating at 1200° C for 4 hours a natural bauxite, crystallographically consisting of gibbsite contaminated with some quartz and TiO_2, the second being γ-Al_2O_3, formed by heating for 4 hours at 400° C a nearly amorphous Boehmite contaminated by some aluminium sulphate (furnished by Brocades, Stheeman, and Pharmacia of Meppel). With those catalysts reaction mixtures were formed which contained respectively 30 and 18 per cent *n*-butenes, calculated on total butenes. From these mixtures the *iso*butene was removed by repeated shaking with the aqueous hydrochloric acid solution, saturated with NaCl as mentioned above. The remaining gas was very carefully fractionated in the Podbielniak column and a middle fraction of butene-2 with a constant boiling point was separated. Its purity was certainly higher than 90 per cent.

Butadiene-1 : 3.

Butadiene-1 : 3 was prepared by dehydration of butylene glycol-1 : 3 by passing it at 400° C with a contact time of 0·5 min over a catalyst prepared by melting a mixture of 350 g NaH_2PO_4 and 110 g crystallized H_3PO_4.[14] The crude product (yield 44 per cent) was purified by repeated distillation from the higher-boiling reaction products.

iso*Butane.*

*iso*Butane was prepared by hydrogenation of a portion of *iso*butene. It was purified by distillation in the Podbielniak column.

Ethylene.

Ethylene, used only in solubility measurements, was prepared by dehydration of ethyl alcohol at 400° C using Al_2O_3 as a catalyst.

All gases were introduced into small 500-ml cylinders, after which air was removed by pumping, the cylinder being cooled in liquid air. This procedure was repeated several times with intermediate periods of heating to room temperature and recooling in liquid air. The vacuum pump could easily reach a pressure of 0·06 mm mercury.

---

* Determined with a mixture of benzene-dichloroethane and calculated with the data of Pahlavouni.[13]

Solubility Measurements.

In order to establish the final procedure of the analysis, the solubilities of various gases in different liquids at 20° C were measured first. These measurements were carried out in the Bunte burette and the solubilities were calculated from the decrease in volume and the final amount of liquid present. The results are given in Table I.

Table I.

Solubility of Several Gaseous Olefins, iso Butane and CO_2, in ml/100 ml liquid at 20° C and Atmospheric Pressure.

Olefin.	Liquid.					
	Water.	H_2O saturated with NaCl.	HCl 1 : 1 saturated with [a]			
			—	NaCl.	$NaNO_3$.	NaH_2PO_4.
Propene	10·4 ± 1·0 [c]	1·7 ± 0·2 [d]	8·2 ± 0·4 [c]	7·8 ± 0·5 [d]	8·2 ± 0·7 [c]	6·4 ± 0·2 [e]
Butene-1	8 3 ± 0·5 [c]	0·5 [b]	—	8·5 ± 0·4 [f]	—	—
Butene-2	9·3 [b]	0·5 [b]	—	9·6 ± 0·7 [e]	—	—
*iso*Butene	11·3 ± 0·1 [e]	0·6 ± 0·1 [e]	—	totally	—	—
Butadiene	—	—	—	19·0 ± 0·8 [d]	—	—
*iso*Butane	—	—	—	1·3 ± 0·5 [f]	—	—
Ethylene	—	—	—	7·0 ± 0·2 [e]	—	—
CO_2	—	—	—	40·1 [b]	—	—

[a] In these cases a correction of —0·4 ml/100 ml gas was applied in connexion with the vapour pressure of the liquid (probably HCl).
[b] Only one determination.
[c] Average of two determinations.
[d] Average of three determinations.
[e] Average of six determinations.
[f] Average of seven determinations.

In view of these results it is evident that the gas should be sampled using a saturated NaCl solution as a liquid, since the solubility of many olefins in water is considerably higher.

It is also clear that in the case of propene, addition of NaCl to the aqueous hydrochloric acid solution does not have a notable influence on the solubility, which for olefins is in general fairly considerable. Substitution of the NaCl by other salts like $NaNO_3$ and NaH_2PO_4 did not result in a negligible solubility. Though not actually tested, the same will probably hold good for the other olefins. Nevertheless, the investigation presented here was carried out with the reagent saturated with NaCl. The high solubility values of the non-reacting gases suggest the necessity of applying a solubility correction in the procedure of the analysis. An endeavour to avoid this by neutralizing the acid at the end of the analysis failed as it was impossible to introduce sufficient alkali without a previous removal of too great an amount of reagent; moreover, the heat evolved during the neutralization caused the evolution of an amount of non-hydrocarbon gas (CO_2 and air) from the liquids used.

Analyses.

The analyses were carried out according to the method of Bunte–Jaeger and the following procedure was adopted.

The gas was sampled over a saturated NaCl solution and the volume was measured after the burette had been for 15 minutes in a thermostat kept at 20° C, during which time the pressure was established several times by connecting the burette to the cup, which was filled with liquid to a definite level.* Thereupon the liquid was almost completely removed by means of a water-jet air pump and replaced by the reagent. The burette was then shaken vigorously while care was taken not to heat it by contact with the hands. After certain intervals the diminished pressure resulting from the adsorption of the gas was compensated by introducing more reagent. In the beginning this proved to be necessary after two or three shakings, in order to prevent the entrance of air from the outside on account of the vacuum produced. Afterwards intervals of 2 and finally of 10 minutes' shaking could be used. When the volume of the gas did not alter during one shaking period, the burette was again put in the thermostat for 15 minutes and the volume measured after establishment of the pressure. Then the burette was again shaken for 10 minutes after which time it was again placed in the thermostat and the volume measured after 15 minutes. This procedure was repeated till the gas volume became constant.

This method of analysis was tested with several binary mixtures prepared in the burette before analysis. The results are given in the Tables II to IV.

A comparison of the end volumes after shaking (col. 5) and also after application of a correction to the end volume as a consequence of the HCl vapour pressure (col. 7) with the original intake volumes of the non-reacting component (col. 2) shows that the former values are, in general, much too low, leading to too high *iso*butene concentrations (col. 11).

Application of solubility corrections deduced from Table I, however, results in too high "corrected end volumes" (col. 9). This is due to the *tert*-butyl chloride formed during the reaction, which possesses a certain vapour pressure and possibly also influences the solubility of the non-reacting gas. It is, however, found that the differences between the corrected and the expected end volumes (col. 12) show a dependence on the percentage of *iso*butene present. This becomes clear by reference to the Figs. 1 to 5, in which the deviation is plotted against the *iso*butene concentrations calculated from the direct readings after shaking (col. 11). From these graphs it is seen that at low *iso*butene concentrations the deviation increases linearly with the *iso*butene concentration, afterwards remaining constant for a certain period, and finally increasing sharply at high *iso*butene concentrations. A possible explanation for this behaviour is found in the slow increase in vapour pressure of the *tert*-butyl chloride formed with increasing *iso*butene content when small amounts of *iso*butene are present, possibly accentuated by the solubility of the chloride in the aqueous phase, followed by a period of constant maximum vapour pressure in cases when more *iso*butene is present. The sharp and large increase at very high *iso*butene concentrations is a consequence of the fact that the total solubility correction has also been applied in cases where none, or very small amounts, of the non-reacting gas were present, in order to make the

* Though definite differences in solubility in the sampling liquid may exist between components of a mixture (see Table I), changes in the gas composition during sampling may be neglected as the rate of solution without shaking is very low.

TABLE II.

Analyses of Mixtures of iso*Butene and Propene.*

Expt. no.	Intake, ml.			End vol, ml.		Corrections, ml.		Corr end vol, ml.	% *i*-C_4 in intake.		ΔC_4 vol (from 2, 9).	Solub. corr C_3 in ml/100 ml from 2, 5, 6.	Method 1.				Method 2.			
	C_3	*i*-C_4.	Total.	Gas.	Liq.	HCl vap. press.	C_3 solubility.		Theor.	Calc from 5.			Final corr. Fig. 1, ml.	Corr end vol, ml, from 9, 14.	Calc. % *i*-C_4.	% Deviation.	Corr ml from 13, av.	Corr end vol, ml, from 5, 18.	Calc % *i*-C_4.	% Deviation.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	60·2	6·9	67·1	56·2	62·8	−0·2	+4·9	60·9	10·3	16·2	−0·7	6·4	−0·8	60·1	10·4	+1·0	+3·3	59·5	11·3	+9·7
2	63·2	9·7	72·9	59·5	57·5	−0·2	+4·5	63·8	13·3	18·4	−0·6	6·4	−0·9	62·9	13·7	+3·0	+3·0	62·5	14·2	+6·8
3	50·9	12·1	63·0	46·8	72·2	−0·2	+5·6	52·2	19·2	25·7	−1·3	5·7	−1·3	50·9	19·2	0·0	+3·8	50·6	19·7	+2·6
4	55·6	15·7	71·3	52·2	64·8	−0·2	+5·1	57·1	22·0	26·8	−1·5	5·2	−1·4	55·7	21·9	−0·4	+3·4	55·6	22·0	0·0
5	44·0	26·4	70·4	40·3	78·7	−0·2	+6·1	46·2	37·5	42·7	−2·2	4·7	−2·0	44·2	37·2	−0·8	+4·2	44·5	36·8	−1·9
6	42·8	27·4	70·2	38·4	78·6	−0·2	+6·1	44·3	39·0	45·3	−1·5	5·6	−2·0	42·3	39·7	+1·8	+4·2	42·6	39·3	+0·8
7	28·4	42·4	70·8	23·4	95·6	−0·1	+7·5	30·8	59·9	67·0	−2·4	5·2	−2·0	28·7	59·4	−0·8	+5·1	28·5	59·7	−0·3
8	27·4	44·1	71·5	21·6	95·4	−0·1	+7·4	28·9	61·7	69·8	−1·5	6·1	−2·0	26·9	62·4	+1·1	+5·1	26·7	62·7	+1·6
9	14·3	55·3	69·6	9·0	110·0	0·0	+8·6	17·6	79·4	87·1	−3·3	4·8	−2·1	15·5	77·7	−2·2	+5·8	14·8	78·7	−0·9
10	12·6	62·6	75·2	8·8	108·2	0·0	+8·4	17·2	83·2	88·3	−4·6	3·5	−2·2	15·0	80·1	−3·7	+5·7	14·5	80·9	−2·8
11	0·0	72·2	72·2	0·4	118·6	0·0	+9·2	9·6	100·0	99·5	−9·6	— *	−9·6	0·0	100·0	0·0	+6·3	6·7	90·7	−9·3
12	5·3	81·5	86·8	1·6	115·4	0·0	+9·0	10·6	93·9	98·2	−5·3	3·2 *	−5·2	5·4	93·8	−0·1	+6·1	7·7	91·1	−3·0
13	10·7	59·0	69·7	4·6	114·4	0·0	+8·9	13·5	84·7	93·4	−2·8	5·3	−2·8	10·7	84·6	−0·1	+6·1	10·7	84·5	−0·2
14	7·8	66·6	74·4	5·8	113·2	0·0	+8·8	14·6	89·5	92·2	−6·8	(1·8) *	−2·6	12·0	83·9	−6·2	+6·0	11·8	84·1	−6·0
15	14·6	62·2	76·8	8·4	108·6	0·0	+8·5	16·9	81·0	89·1	−2·3	5·7	−2·2	14·7	80·9	−0·1	+5·8	14·2	81·5	+0·6
16	6·8	59·9	66·7	2·2	116·8	0·0	+9·1	11·3	89·8	96·7	−4·5	(3·9) *	−4·0	7·3	89·0	−0·9	+6·2	8·4	87·4	−2·7
17	14·2	58·2	72·4	7·8	109·2	0·0	+8·5	16·3	80·4	90·3	−2·1	5·9	−2·4	13·9	80·8	+0·5	+5·8	13·6	81·2	+1·0
18	18·9	52·0	70·9	12·8	106·2	0·0	+8·3	21·1	73·4	82·0	−2·2	5·7	−2·0	19·1	73·1	−0·4	+5·6	18·4	74·0	+0·8
19	35·6	35·0	70·6	31·0	86·0	−0·1	+6·7	37·6	49·6	56·1	−2·0	5·3	−2·0	35·6	49·6	0·0	+4·5	35·5	49·7	+0·2
20	54·5	15·7	70·2	51·2	69·8	−0·2	+5·5	56·5	22·4	27·1	−2·0	4·7	−1·4	55·0	21·6	−3·6	+3·7	54·9	21·8	−2·7
21	48·4	20·3	68·7	44·5	72·5	−0·2	+5·7	50·0	29·5	35·2	−1·6	5·3 av. 5·3	−1·8	48·1	30·0	+1·7	+3·8	48·3	29·7	+0·7

* These figures are without value as the liquid is not saturated with C_3.

TABLE III.

Analyses of Mixtures of iso*Butene and* n-*Butene*-1.

Expt. no.	Intake, ml.			End vol, ml.		Corrections, ml.		Corr end vol, ml.	% *i*-C_4 in intake.		Δn-C_4-1 vol (from 2, 9).	Solub. correct, *n*-C_4-1 in ml/100 ml from 2, 5, 6.	Method 1.				Method 2.			
	n-C_4-1.	*i*-C_4.	Total.	Gas.	Liquid.	HCl vap. pressure.	*n*-C_4-1 solubility.		Theor.	Calc from 5.			Final corr. Fig. 2, ml.	Corr end vol, ml. from 9, 14.	Calc. % *i*-C_4.	% Deviation.	Corr. ml. from 13 av.	Corr end vol, ml. from 5, 18.	Calc % *i*-C_4.	% Deviation.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1 *	29·4	39·1	68·5	24·7	94·3	−0·1	+ 8·0	32·6	57·1	63·9	− 3·2	5·0	− 2·0	30·6	55·3	−3·2	+5·7	30·4	55·6	− 2·6
2	44·0	26·6	70·6	39·9	77·1	−0·2	+ 6·5	46·2	37·7	43·5	− 2·2	5·3	− 1·9	44·3	37·3	−1·1	+4·7	44·6	36·8	− 2·4
3	14·2	55·2	69·4	7·3	111·7	−0·0	+ 9·5	16·8	79·5	89·5	− 2·6	6·2	− 2·1	14·7	78 8	−0·9	+6·8	14·1	79·7	+ 0·3
4	17·4	50·4	67·8	10·3	108·7	−0·0	+ 9·2	19·5	74·3	84·8	− 2·1	6·5	− 2·0	17·5	74·2	−0·1	+6·6	16·9	75·1	+ 1·1
5	10·2	60·6	70·8	3·2	113·8	−0·0	+ 9·7	12·9	85·6	95·5	− 2·7	6·1	− 2·7	10·2	85·6	0·0	+6·9	10·1	85·7	+ 0·1
6	27·8	41·6	69·4	21·5	97·5	−0·1	+ 8·3	29·7	59·9	69·0	− 1·9	6·5	− 2·0	27·7	60·1	+0·3	+5·9	27·4	60·3	+ 1·0
7	42·2	29·1	71·3	37·5	79·5	−0·2	+ 6·8	44·1	40·8	47·4	− 1·9	5·9	− 2·0	42·1	41·0	+0·5	+4·8	42·3	40·7	− 0·2
8	4·1	67·2	71·3	0·6	118·4	−0·0	+10·0	10·6	94·2	99·2	− 6·5	(2·9) †	− 6·5	4·1	94·2	0·0	+7·2	7·8	89·1	− 5·4
9	63·9	4·6	68·5	59·8	57·2	−0·2	+ 4·9	64·5	6·7	12·7	− 0·6	7·2	− 0·5	64·0	6·6	−1·5	+3·5	63·3	7·6	+13·4
10	0·0	72·2	72·2	0·4	118·6	−0·0	+10·1	10·5	100·0	99·6	−10·5	— †	−10·5	0·0	100·0	0·0	+7·2	7·6	89·5	−10·5
11	56·8	12·4	69·2	52·3	66·7	−0·2	+ 5·7	57·8	18·0	24·4	− 1·0	6·7	− 1·1	56·7	18·1	+0·6	+4·1	56·4	18·5	+ 2·8
12	47·4	19·2	66·6	42·9	74·1	−0·2	+ 6·3	49·0	28·8	35·6	− 1·6	6·1 av. 6·1	− 1·5	47·5	28·7	−0·4	+4·5	47·4	28·8	0·0

* During this experiment the burette is probably heated up by direct contact with the hands. After cooling in the thermostat it was not shaken again.
† These figures are without value as the liquid is not saturated with *n*-C_4-1.

TABLE IV.

Analyses of Mixtures of iso*Butene and* n*-Butene-2.*

Expt. no.	Intake, ml.			End vol, ml.		Corrections, ml.		Corr end vol, ml.	% *i*-C_4 in intake.		Δn-C_4-2 vol from 2, 9.	Solub. corr *n*-C_4-2, ml/100 ml from 2, 5, 6.	Method 1.				Method 2.			
	n-C_4-2.	*i*-C_4.	Total.	Gas.	Liquid.	HCl vap pressure.	*n*-C_4-2 solubility.		Theor.	Calc from 5.			Final corr. Fig. 3, ml.	Corr end vol, ml, from 9, 14.	Calc, % *i*-C_4.	% Deviation.	Corr ml from 13, av.	Corr end vol, ml, from 5, 18.	Calc. % *i*-C_4.	% Deviation
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	59·8	16·3	76·1	56·0	61·5	−0·2	+ 5·9	61·7	21·4	26·4	− 1·9	6·2	− 1·3	60·4	20·6	−3·8	+4·2	60·2	20·9	− 2·4
2	59·3	27·0	86·3	56·2	60·8	−0·2	+ 5·8	61·8	31·3	34·9	− 2·5	5·1	− 1·8	60·0	30·5	−2·6	+4·1	60·3	30·1	− 3·9
3	54·5	28·0	82·5	50·5	66·5	−0·2	+ 6·4	56·7	33·9	38·8	− 2·2	6·0	− 2·0	54·7	33·7	−0·6	+4·5	55·0	33·0	− 2·7
4	44·5	33·0	77·5	39·0	81·0	−0·2	+ 7·8	46·6	42·6	49·7	− 2·1	6·8	− 2·0	44·6	42·5	−0·2	+5·5	44·5	42·6	0·0
5	43·0	36·2	79·2	37·4	79·6	−0·1	+ 7·6	44·9	45·7	52·8	− 1·9	7·0	− 2·0	42·8	46·0	+0·6	+5·4	42·8	46·0	+ 0·7
6	27·4	43·0	70·4	19·8	100·2	−0·1	+ 9·6	29·3	61·1	71·9	− 1·9	7·6	− 2·0	27·3	61·2	+0·2	+6·8	26·6	62·2	+ 1·8
7	18·6	54·4	73·0	10·4	106·6	0·0	+10·2	20·6	74·5	85·8	− 2·0	7·7	− 2·0	18·6	74·5	0·0	+7·2	17·6	75·9	+ 1·9
8	9·4	79·0	88·4	2·5	117·5	0·0	+11·3	13·8	89·4	97·2	− 4·4	5·9	− 4·4	9·4	89·4	0·0	+8·0	10·5	88·1	− 1·4
9	62·4	13·2	75·6	58·2	58·8	−0·2	+ 5·6	63·6	17·4	23·0	− 1·2	7·1	− 1·1	62·5	17·3	−0·6	+4·0	62·2	17·7	+ 1·7
10	50·4	7·6	58·0	44·2	75·8	−0·2	+ 7·3	51·3	13·1	23·8	− 0·9	8·2	− 1·2	50·1	13·6	+3·8	+5·1	49·3	15·0	+13·5
11	0·0	72·2	72·2	0·4	118·6	0·0	+11·4	11·8	100·0	99·5	−11·8	— * av. 6·8	−11·8	0·0	100·0	0·0	+8·0	8·4	88·4	−13·0

* This figure is without value as the liquid is not saturated with *n*-C_4-2.

TABLE V.

Analyses of Mixtures of iso*Butene and Butadiene* (C^4).

Expt. no.	Intake, ml.			End vol, ml.		Corrections, ml.		Corr end vol, ml	% *i*-C_4 in intake.		ΔC_4 vol from 2, 9.	Solub. corr C_4 in ml/100 ml liq from 2, 5, 6.	Method 1.				Method 2.			
	C_4.	*i*-C_4.	Total.	Gas.	Liquid.	HCl vap. pressure.	C_4 solubility.		Theor.	Calc from 5.			Final corr. Fig. 4, ml.	Corr end vol. ml, from 9, 14.	Calc. % *i*-C_4.	% Deviation.	Corr ml from 13 av.	Corr end vol. ml, from 5, 18.	Calc. % *i*-C_4.	% Deviation.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	46·5	22·3	68·8	31·6	86·4	−0·1	16·4	47·9	32·4	54·0	− 1·4	17·3	− 1·4	46·5	32·4	0·0	+15·0	46·6	32·3	− 0·3
2	35·2	46·0	81·2	19·2	97·8	−0·1	18·6	37·7	56·6	76·4	− 2·5	16·4	− 2·3	35·4	56·4	− 0·4	+17·0	36·2	55·4	− 2·1
3	23·0	46·8	69·8	5·5	112·5	0·0	21·4	26·9	67·0	92·1	− 3·9	15·6	− 3·9	23·0	67·0	0·0	+19·6	25·1	64·0	− 4·5
4	9·4	62·9	72·3	0·7	116·3	0·0	22·1	22·8	87·0	99·0	−13·4	(7·5) *	−13·0	9·8	86·4	− 0·7	+20·2	20·9	71·1	−18·3
5	0·0	72·2	72·2	0·4	118·6	0·0	22·5	22·9	100·0	99·6	−22·9	— *	−23·0	−0·1	100·1	+ 0·1	+20·6	21·0	70·9	−29·1
6	16·8	54·6	71·4	2·3	114·7	0·0	21·8	24·1	76·5	96·8	− 7·3	12·6	− 7·0	17·1	76·1	− 0·5	+20·0	22·3	68·8	−10·1
7	42·1	30·5	72·6	21·2	99·8	−0·1	19·0	40·1	42·0	70·8	+ 2·0	20·9	− 2·0	30·1	58·5	+39·3	+17·4	38·6	46·8	+11·4
8	40·2	29·9	70·1	21·8	95·2	−0·1	18·1	39·8	42·6	68·9	+ 0·4	19·3	− 1·9	37·9	45·9	+ 7·7	+16·6	38·4	45·2	+ 6·1
9	47·4	27·0	74·4	32·4	88·6	−0·1	16·8	49·1	36·3	56·5	− 1·7	16·9	− 1·5	47·6	36·0	− 0·8	+15·4	47·8	35·8	− 1·4
10	54·2	18·1	72·3	40·8	78·2	−0·2	14·8	55·4	25·0	43·6	− 1·2	17·1	− 1·2	54·3	24·9	− 0·4	+13·6	54·4	24·8	− 0·8
11	37·4	31·4	68·8	21·0	96·0	−0·1	18·2	39·1	45·7	69·5	− 1·7	17·1	− 1·9	37·2	45·9	+ 0·4	+16·7	37·7	45·2	− 1·1
12	51·8	15·9	67·7	34·4	84·6	−0·1	16·1	50·4	23·5	49·2	+ 1·4	20·6	− 1·3	49·1	27·5	+17·0	+14·7	49·1	27·5	+17·0
13	56·7	9·2	65·9	43·8	73·2	−0·2	13·9	57·5	14·0	33·5	− 0·8	17·6 av. 17·4	− 0·9	56·6	14·1	+ 0·7	+12·7	56·5	14·3	+ 2·1

* These figures are without value as the liquid is not saturated with C_4.

TABLE VI.

Analyses of Mixtures of iso*Butene and* iso*Butane.*

Expt. no.	Intake, ml.			End vol, ml.		Corrections, ml.		Corr. end vol, ml.	% *i*-C_4 in intake.		Δ*i*-Butane vol from 2, 9.	Solub. corr *i*-butane, ml/100 ml liq. from 2, 5, 6.	Method 1.				Method 2.			
	i-Butane.	*i*-C_4.	Total.	Gas.	Liquid.	HCl vap pressure.	*i*-Butane solubility.		Theor.	Calc from 5.			Final corr. Fig. 5, ml.	Corr end vol, ml, from 9, 14.	Calc. % *i*-C_4.	% Deviation.	Corr. ml from 13 av.	Corr end vol, ml, from 5, 18.	Calc, % *i*-C_4.	% Deviation.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	0·0	72·2	72·2	0·4	118·6	0·0	+1·5	1·9	100·0	99·5	−1·9	— *	−1·9	0·0	100·0	0 0	0 0	0·4	99·4	−0·6
2	3·6	67·5	71·1	3·5	115·5	0·0	+1·5	5·0	94·9	95·1	−1·4	0·1	−1·4	3·6	94·9	0·0	0·0	3·5	95·1	+0·2
3	33·6	31·6	65·2	33·9	83·1	−0·2	+1·1	34·8	48·5	48·0	−1·2	−0·4	−1·3	33·5	48·6	+0·2	0·0	33·9	48·0	−1·0
4	3·6	65·8	69·4	3·6	115·4	0·0	+1·5	5·1	94·8	94·8	−1·5	0·0	−1·4	3·7	94·7	−0·1	0·0	3·6	94·8	0·0
5	39·9	39·3	79·2	40·4	76·6	−0·2	+1·0	41·2	49·6	49·0	−1·3	−0·6	−1·3	39·9	49·6	0·0	0·0	40·4	49·0	−1·2
6	19·5	49·1	68·6	19·6	99·4	−0·1	+1·3	20·8	71·6	71·4	−1·3	−0·1	−1·3	19·5	71·6	0·0	0·0	19·6	71·4	−0·3
7	14·8	65·4	80·2	15·0	102·0	−0·1	+1·3	16·2	81·5	81·3	−1·4	−0·2	−1·3	14·9	81·4	−0·1	0·0	15·0	81·3	−0·2
8	50·3	20·3	70·6	50·4	68·6	−0·2	+0·9	51·1	28·7	28·6	−0·8	−0·1	−0·8	50·3	28·7	0·0	0·0	50·4	28·6	−0·4
9	55·0	14·6	69·6	55·0	62·0	−0·2	+0·8	55·6	21·0	21·0	−0·6	0·0	−0·6	55·0	21·0	0·0	0·0	55·0	21·0	0·0
10	64·2	7·2	71·4	64·2	54·8	−0·3	+0·7	64·6	10·1	10·1	−0·4	0·0	−0·3	64·3	9·9	−2·0	0·0	64·2	10·1	0·0
11	67·5	3·5	71·0	67·5	49·5	−0·3	+0·6	67·8	4·9	4·9	−0·3	0·0	−0·2	67·6	4·8	−2·0	0·0	67·5	4·9	0·0
12	58·0	5·4	63·4	57·8	61·2	−0·2	+0·8	58·4	8·5	8·8	−0·4	0·3 av. 0·0	−0·3	58·1	8·4	−1·2	0·0	57·8	8·8	+3·5

* This figure is without value as the liquid is not saturated with *i*-Butane.

method and calculation of the analysis uniform. So it does not represent a physical reality, but is simply a consequence of the fact that the correction for the solubility of non-reacting components is larger than the amount of these components present. The method of plotting the final deviation against the calculated *iso*butene concentration is of course not very exact, but it makes the calculation of a final correction in each case possible. This is done using the graphs which represent the average course of the deviation (col. 14). These figures are used in calculating the final corrected end volume (col. 15) and the *iso*butene content of the intake gas (col. 16). The deviations from the true *iso*butene contents in percentages are given in col. 17.

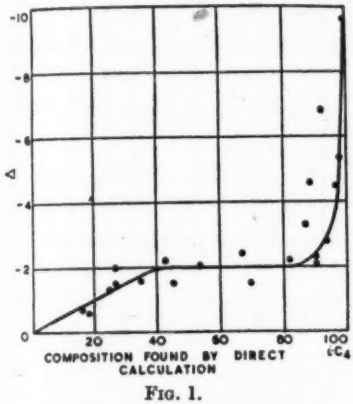


FIG. 1.

MIXTURES OF *iso*BUTENE AND PROPENE.

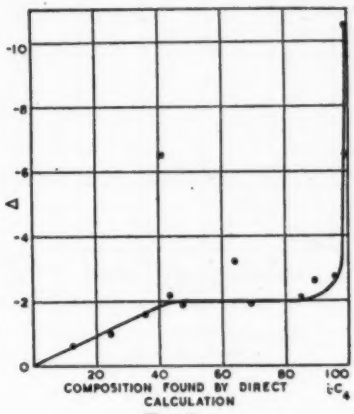


FIG. 2.

MIXTURES OF *iso*BUTENE AND *n*-BUTENE-1.

In connexion with the intricacy of this method of calculation (method 1) another method was investigated. In this second method all previous corrections were combined into one new correction which was given the character of a solubility correction, calculated from the results and listed in col. 13. An average figure deduced from the separate results (except the figures in brackets) is used in calculating the *iso*butene contents of the intake gases (col. 20).

From these tables it transpires that, in general, method 1 gives the most reliable results, especially in cases of small *iso*butene contents. The extremely good agreement between the theoretical and the calculated figures at high *iso*butene contents is somewhat exaggerated, as the position of the final correction curves in the figures are largely deduced from the same measurements. On the other hand, method 2 gives very divergent results * in the same cases and also in the cases of small *iso*butene contents, when the mixture is at least composed of non-reacting gases having a

* Another method of calculation consistent with method 2, but in which the correction for the HCl-vapour pressure is applied separately gives results identical with those of method 2.

considerable solubility (in the case of *iso*butane the differences between the results of the methods are much smaller).

These results necessarily lead to the conclusion that method 1 is the best method in all cases, whereas the simplicity of method 2 can be advantageous

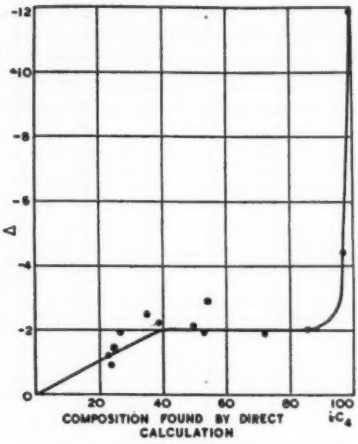


FIG. 3.

MIXTURES OF *iso*BUTENE AND *n*-BUTENE-2.

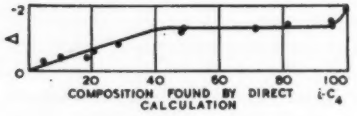


FIG. 5.

MIXTURES OF *iso*BUTENE AND *iso*BUTANE.

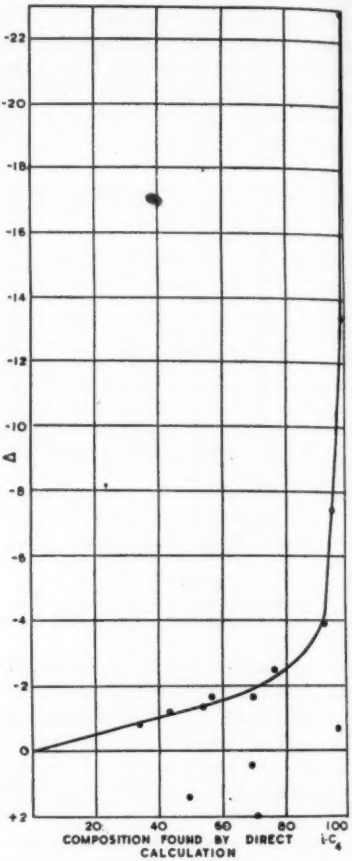


FIG. 4.

MIXTURES OF *iso*BUTENE AND BUTADIENE.

in cases where moderate amounts of *iso*butene are present. In these cases deviations in the calculated *iso*butene concentrations are in general of the order of max 1 and 2 per cent respectively.*

The possible high discrepancies at high *iso*butene concentrations also when

* Small deviations at low *iso*butene concentrations result in fairly high relative deviations.

TABLE VII.

Analyses of Mixtures of iso*Butene and Propene with Addition of Indifferent Gas.*

Expt. no.	Intake, ml.					% Indifferent gas.	End vol, ml.			HCl vapour pressure corr.	Corr end vol, ml.	ΔC_3-volume.		% *i*-C_4 on total hydrocarbon.		% Deviation.
	C_3.	*i*-C_4.	H_2.	Air.	Total.		Gas.	Liq.	Hydrocarbon.			From 2, 12.	From 2, 10.	Theor.	Calc. from 2 + 3, 10.	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	6·2	28·4	33·8	—	68·4	49·4	39·5	79·5	5·7	−0·2	5·5	+0·7	+0·5	82·1	83·5	+1·7
2	0·0	36·2	41·9	—	78·1	53·6	42·2	74·8	0·3	−0·2	0·1	−0·1	−0·3	100·0	99·2	−0·8
3	3·2	30·8	33·0	—	67·0	49·3	36·3	82·7	3·3	−0·1	3·2	0·0	−0·1	90·6	90·3	−0·3
4	8·8	26·4	43·3	—	78·5	55·1	51·8	65·2	8·5	−0·2	8·3	+0·5	+0·3	75·0	75·8	+1·1
5	0·0	33·9	—	33·0	66·9	49·3	33·2	85·8	0·2	−0·1	0·1	−0·1	−0·2	100·0	99·4	−0·6
6	5·9	29·1	—	34·8	69·8	49·9	40·2	76·3	5·4	−0·2	5·2	+0·7	+0·5	83·1	84·6	+1·8
												av. +0·3	av. +0·1			

TABLE VIII.

Analyses of Mixtures of iso*Butene and Butene*-1 *with Addition of Air.*

Expt. no.	Intake, ml.					% Air.	End vol, ml.			HCl vap pressure corr.	Corr end vol, ml.	Δn-C_4-1 vol.		% *i*-C_4 on total hydrocarbon.		% Deviation.
	n-C_4-1.	*i*-C_4.	Total hydrocarbon.	Air.	Total.		Gas.	Liquid.	Hydrocarbon.			From 2, 12.	From 2, 10.	Theor.	Calc. from 4, 10.	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	4·6	29·8	34·4	33·9	68·3	49·6	38·3	80·7	4·4	−0·2	4·2	+0·4	+0·2	86·6	87·2	+0·7
2	14·2	21·0	35·2	32·8	68·0	48·2	46·8	70 2	14 0	−0·2	13·8	+0·4	+0·2	59·7	60·2	+0·8
3	5·8	29·7	35·5	33·7	69·2	48·7	39·2	79·8	5·5	−0·2	5·3	+0·5	+0·3	83·7	84·5	+0·9
4	2·8	32·2	35·0	32·7	67·7	48·3	35·7	81·3	3·0	−0·1	2·9	−0·1	−0·2	92·0	91·4	−0·7
												av. +0·3	av. +0·1			

TABLE IX.

Analyses of Mixtures of iso-Butene and Butadiene (C_4) with Addition of Air.

Expt. no.	Intake, ml.				% i-C_4 on total hydrocarbon.	% Air.	End vol., ml.			ΔC_4 vol. from 2, 11.	Solub corr C_4 in ml/100 ml liq. from 10, 12.	Method 1.				Method 2.			
	C_4.	i-C_4.	Total hydro-carbon.	Air.	Total.			Gas.	Liquid.	Hydro-carbon.			Corr in ml from 12 av.	Corr end vol, ml, from 11, 14.	Calc. % i-C_4.	% Deviation.	Corr, ml, from 13 av.	Corr end vol, ml, from 11, 18.	Calc. % i-C_4.	% Deviation.
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	10·1	25·0	35·1	31·9	67·0	71·2	47·6	39·3	79·7	7·4	+2·7	3·4	+3·0	10·4	70·4	− 1·1	+3·1	10·5	70·1	−1·5
2	6·5	28·1	34·6	34·6	69·2	81·2	50·0	39·3	77·7	4·7	+1·8	2·3	+3·0	7·7	77·7	− 4·3	+3·0	7·7	77·7	−4·3
3	10·4	27·0	37·4	30·6	68·0	72·2	45·0	37·9	81·1	7·3	+3·1	3·8	+3·0	10·3	72·5	+ 0·4	+3·2	10·5	71·9	−0·4
4	16·6	19·6	36·2	32·4	68·6	54·1	47·2	44·6	72·4	12·2	+4·4	6·1	+3·0	15·2	58·0	+ 7·2	+2·8	15·0	58·6	+8·3
											av. +3·0	av. 3·9								

applying method 1, induced us to start another investigation in which the gas was diluted by an indifferent gas. Table I shows that CO_2 cannot be used as such. Investigations were carried out with hydrogen and air.

With binary mixtures of *iso*butene with small amounts of propene and butene-1 (Tables VII and VIII) it was found that the differences between the directly measured end volumes and the intake quantity of non-reacting gas was quite negligible (viz., av. 0·1 ml (col. 14) and av. 0·3 ml when applying the HCl vapour pressure correction (col. 13)). *iso*Butene concentrations calculated directly from the end volumes gave fairly accurate values (col. 16).* The intake gas was in all cases diluted with an approximately equal amount of indifferent gas. This simple behaviour proved to prevail no longer when mixtures of *iso*butene and butadiene were investigated. The end values after shaking were always too low. Two methods of calculation were applied. The first used an average correction deduced from col. 12, the second method made use of an average solubility correction without a separate HCl vapour pressure correction having been applied. The two methods of calculation do not differ very much in accuracy, which in all cases is rather poor. More measurements will be necessary to develop a more accurate method of analysis in this special case. Whereas mixtures of *iso*butene and butadiene do not occur frequently, the inaccuracy found in this case is no impediment to the practical application of the method described.

The author wishes to express his sincere thanks to Dr Visser of N.V. De Bataafsche Petroleum Maatschappij for his valuable comments on this manuscript.

Laboratory of Chemical Engineering
of the Technical University,
Delft, Holland.

References.

[1] Michael, A., and Brunel, R. F. *Am. Chem. J.*, 1909, **41**, 118;
Coffin, C. C., Sutherland, H. S., and Maass, O. *Canad. J. Res.*, 1930, **2**, 627;
Piotrowski, W. J., and Winkler, J. *J. Inst. Petrol. Tech.*, 1931, **17**, 325;
Leendertse, J. J., Tulleners, A. J., and Waterman, H. I. *Rec. trav. chim.*, 1933, **52**, 515; 1934, **53**, 715;
Waterman, H. I., Leendertse, J. J., and de Kok, A. J. *Rec. trav. chim.*, 1934, **53**, 1151;
For a survey see Leendertse, J. J., and Waterman, H. I. *Proc. World Petrol. Congr.*, Paris, 1937;
Leendertse, J. J. Thesis, Delft 1938. *Rec. trav. chim.*, 1938, **57**, 795.
[2] Dobryansky, A. *Neft. Slant. Khoz.*, 1925, **9**, 565; *Chem. Zentr.*, 1926, **1**, 2220;
Davis, H. S. *J. Amer. chem. Soc.*, 1919, **41**, 118; 1928, **50**, 2780;
Davis, H. S., and Schuler, R. *J. Amer. chem. Soc.*, 1930, **52**, 721;
Markowitsch, M. B., and Moot, W. G. *Neft. Khoz.*, 1930, **19**, 604; *Chem. Zentr.*, 1931, **1**, 2454; *Nat. Petrol. News*, 1931, **23** (41), 33; (42), 72;
Matuszak, M. P. *Industr. Engng Chem. Anal.*, 1938, **10**, 354.
[3] McMillan, W. A. *Industr. Engng Chem. Anal.*, 1937, **9**, 511.
[4] Newton, A., and Buckler, E. J. *Industr. Engng Chem. Anal.*, 1940, **12**, 251.

* In this connexion it is worth while to pay attention to the concordant results obtained by Dr Visser with cracking gases, in which the saturated hydrocarbon gas plays the rôle of the inert diluent.

[5] Washburn, H. W., Wiley, H. F., and Rock, S. M. *Industr. Engng Chem. Anal.*, 1943, **15**, 541.
[6] Barnes, R. B., Liddel, U., and Williams, V. Z. *Industr. Engng Chem. Anal.*, 1943, **15**, 659.
[7] Keulemans, A. I. M. Thesis, Delft 1942, p. 37. Unpublished method worked out by Dr G. H. Visser at B.P.M. laboratory, Amsterdam.
[8] Vanino, L. "Handbuch der präparativen Chemie," vol. 2, p. 6. Stuttgart 1937.
[9] Timmermans, J., and Delcourt, Y. *J. chim. phys.*, 1934, **31**, 85.
[10] Parks, G. S., Warren, G. E., and Greene, E. S. *J. Amer. chem. Soc.*, 1935, **57**, 616.
[11] Senderens, J. B. *Bull. Soc. Chim.* (*Paris*), 1911, **9**, 373.
[12] Houtman, J. P. W., van Steenis, J., and Heertjes, P. M. *Rec. trav. chim.*, 1946, **65**, 781.
[13] Pahlavouni, E. *Bull. Soc. Chim. Belg.*, 1927, **36**, 533.
[14] Ellis, C. "The Chemistry of Petroleum Derivatives," vol. I, p. 634.

LUBRICATING OIL TESTING IN ENGINES.

By R. Stansfield (Fellow) and J. C. Cree.

Summary.

An increasing use is being made of bench tests of oils in engines for the purpose of grading and, in a few cases, an oil specification includes such a test or tests. There are recognized tests only for certain H.D. oils, but it should be possible to develop others to meet requirements in respect of normal and premium grades and also special H.D. qualities for engines still in the experimental stage.

An account is given of the results of standard tests in the Caterpillar single-cylinder diesel engine and in the Chevrolet petrol engine, and these are discussed in comparison with chemical laboratory inspection data. Lack of significance of the latter led to a series of Chevrolet tests in which bearing weight losses were obtained at intervals during the run and the form of the corrosion curves determined. It was shown, however, that even when the breakdown time of the oil was known it still could not be reproduced satisfactorily by tests of the unused oil in the laboratory.

The use of engine tests of lubricating oils leading to ring sticking is discussed and preference is given to ratings in terms of quantities and nature of deposits during runs which are not continued to the point of ring stick.

The need for reliable methods for determining whether a used additive type oil is still active is emphasized and suggestions are made for experimental work.

Notes are included regarding the precautions to be adopted to obtain satisfactory life and freedom from mechanical trouble with the Chevrolet engines.

The difficulty in predicting, with any accuracy, the probable behaviour of a lubricating oil in an engine from results of chemical and physical laboratory tests has been recognized for upwards of 20 years. This has led many laboratories to adopt bench tests of oils in engines as a means of grading them, but in the past the tendency has been for each laboratory to apply its own operating conditions and develop its own technique and interpretation of results using various types of engines. Such tests have not, however, been included in specifications until recently, and they still apply only to oils made to meet certain service requirements in the U.S.A., and which have to be examined in engines to ensure that they meet the needs of a few special and exacting designs.

The use of the high-speed diesel engine for long periods at full load, and the trend towards heavier duty for petrol engines in long distance transport, led to problems which were solved by the introduction of additives to suitably prepared lubricants, and the proving of the new oils involved appropriate engine tests.

All such recognized tests have, in fact, been developed by various engine builders to provide means by which they could give approval to suitable branded oils; only at a later date the U.S. Army, as a major user of engine lubricants, organized the work on a broader basis, and selected a series of five engine tests which had to be passed by any heavy duty lubricant supplied to them.

The U.S. Navy imposed still more stringent acceptance conditions, and subjected U.S. Army approved oils to its own bench and service tests before passing any grade for Naval use.

Current grades of motor oils can be classified into three broad groups; normal types for easy running conditions in both petrol and diesel engines; premium grades which combine, in various degrees, better resistance to bearing corrosion, engine wear, and sludging, and which may or may not have improved detergent properties; and H.D. types which are highly resistant to bearing corrosion, reduce engine wear, and sludging, and are also sufficiently detergent to keep pistons and piston-rings of heavy duty diesel engines clean for long periods of use. In practice these classifications merge into one another, the premium grade requirements, for example, being met in some cases by suitably refined oils without additives, while in other examples anti-corrosive agents may be included. The H.D. category may shortly require the addition of a range, still more detergent in action than has been called for in the past, to provide for a limited number of recent developments in high-speed supercharged and air-cooled diesel engines.

Oils for reciprocating aero engines are also frequently required to pass actual engine tests, and it has been common practice for some time for individual engine builders to make such tests in their own designs of engine.

The basis of engine tests in the laboratory should always be a satisfactory degree of correlation with service behaviour and this at once introduces a very difficult problem. A given make of engine may run under very easy conditions for a certain type of duty during the whole of its working life, while another of identical construction may operate at heavy loads and high speed, with high oil and jacket temperatures, and be quite unsatisfactory when used with a lubricant which would be entirely suitable for the easier duty. Moreover, various designs of engine of approximately the same output and speed may have different lubricating oil requirements because of working differences due, for example, to local metal thicknesses, design of cooling systems, materials of construction, etc, which can either affect the temperature of the oil on the cylinder walls and in the crankcase, or, in the case of bearing materials, alter resistance to attack by corrosion.

It should be possible, after a thorough study of the variables involved, to make use of two suitably designed engines, one petrol and one diesel, as lubricating oil test units when run under various selected conditions, so that any oil could at least be classified as suitable for normal, premium, or heavy duty petrol engine conditions and, when necessary, for use in diesel engines to a required degree of detergency.

It is unnecessary to emphasize that there is not the same need for elaborate engine tests of all engine lubricating oils as there is for octane number tests of petrols and kerosines or ignition quality tests of diesel fuels. Only a fraction of the number of internal combustion engines in use will fail or give serious trouble attributable to the oil, provided they are run on any reputable normal grade. On the other hand, many engines show lower wear, sludge, and general deposit values if additive type oils are used, even when the running conditions are not extreme. It is known, too, that oils graded in a certain order of merit in respect of, say, ring groove carbon formation and piston deposits are not necessarily rated in the same

order when used at much higher or much lower working temperatures, and it is also true that some oils are rated differently in diesel than in petrol engines.

There seems, therefore, to be a definite need for the use of a recognized series of oil tests in engines to serve for research and development purposes and as a yardstick against which service results may, as far as practicable, be compared.

The standardization of such tests would not imply their introduction into all specifications, and the limit to which they ought to be applied in this way should be as a basis for broad general classifications. To give each brand of oil a rating other than a " go/not-go " quality in any specified class would be as irrational as to restrict all petrol engines to three or four designs only, and would tend to limit supplies severely in an entirely unjustifiable manner.

It is not the purpose of this paper to suggest either the design of engines or the precise test conditions necessary to meet various requirements, but it is thought that discussion of some recent results obtained when making specification and other engine tests of lubricating oils may be of value to those interested in the subject.

It has already been pointed out that engine tests should be made in such a way that the results bear a sufficiently close relation to service behaviour as to form a rational guide for the selection of lubricants; engine testing in the field is much too expensive and lengthy to be useable as more than a starting-point for the collection of data, and as a final check on test bed results. Even bench testing ought to be considered as the second stage in the proving of lubricating oils, provided that satisfactory chemical laboratory tests can be devised for rough sorting and the rejection of unsuitable products.

Unfortunately most of the recognized laboratory tests are worthless as a guide to engine response. The viscosity–temperature relationship is one of the few applicable to engine behaviour, and it is now common practice to make some form of corrosion test to determine the resistance of an oil to oxidation and formation of break-down products which can attack metals in common use in high duty engines. These corrosion tests are frequently used for the rough sorting of oils before engine tests are commenced, but little evidence has been produced to show that they correlate with the results of either bench or road tests, and there is a regrettable tendency to place too much reliance on them in their present form. It is now generally recognized that laboratory tests in which the changes taking place in an oil are determined after some form of oxidation serve only to disqualify the poorest grades, and that they may be misleading if their results are applied too strictly.

Far more attention has been given during the last 20 years to testing engine lubricating oils in relation to piston-ring sticking, carbon deposits, piston-skirt varnish, and sludge formation than to any other factors. Early tests were usually directed towards finding the number of hours which an engine would run before a ring stuck, in an attempt to assess the value of the oil in terms of its tendency to stick rings and to form carbon deposits.

Tests of this description are still made in both small and large engines, and particularly for the examination of aviation lubricants. Carefully

conducted co-operative work suggests, however, that the method is of doubtful reproducibility and that the problem could be attacked in a different manner with advantage.

It is difficult to see how tests to ring stick can be very consistent when all the possible variations of conditions which lead to sticking are taken into account. The normal width of a piston-ring may, for example, be 0·125 inch, with a machining allowance which passes a ring 0·1245 inch wide when high precision work is specified. The ring groove for such a ring may have a standard width of 0·127 inch, with a permissible tolerance allowing it to reach 0·128 inch. In such an example there may be as little as 0·002 inch clearance between the ring and the groove, or as much as 0·0035 inch, an increase of 75 per cent above the minimum value.

Considering the complicated series of causes which combine to give ring sticking, it is surprising that ring-stick tests have been given so much attention when run in standard engines. Recent experience has, in fact, shown that even to obtain moderate reproducibility it is necessary that extreme care must be taken when preparing the test unit and selecting the critical working parts.

Certain tests made on air-cooled engines to determine time to ring stick were found to be valueless and hand lapping of the rings was adopted, using a specified grade of lapping compound with the removal of not less than a certain minimum amount of stock, to give each ring a clearance in its groove held to within two or three ten-thousandths of an inch. Cleaning of the metal surfaces after the lapping process and the cleaning of honed cylinder bores was most important. Unless every possible care was taken to clean the rubbing parts thoroughly, time to ring stick tended to be low. Experience showed also that as the cleaning technique improved the engine had to be run longer before completing a test on a given oil. In the authors' opinion, a lapping process is inconsistent with even moderately satisfactory testing by the ring-stick procedure. Any special finish required should be obtained first by accurate machining and then, if necessary, by final surface finishing, using methods which do not fill the grain of ring surfaces, cylinder walls, etc, with particles of abrasive which cannot be washed out.

During the course of the tests referred to it was noticed that if a certain oil gave ring stick in, say, 15 hours on one run and in 25 hours on a check run, the general condition of the piston was much worse after the latter as regards varnish deposits, carbon on the lands, and carbon in the grooves.

It was found later that a series of oils which had been graded in four full-scale aero engine cylinders by the ring-stick method were graded in the same order in the small air-cooled engine if the tests were terminated in a time which only just led to ring stick on the worst oil. The grading was then made in terms of general appearance and bulk of varnish and other deposits on the pistons. It is believed that this demerit type of test is the more reproducible, and, while it may give an occasional stray result by showing lacquering with an oil which does not readily give ring stick, the chance of such strays is very much smaller than that of serious errors when the ring-stick technique is used.

Detergency Tests.

Perhaps the most satisfactory test for detergency developed to date is the L-1-545 specification test for U.S. Army 2-104B oils, made on the Caterpillar single-cylinder diesel engine. If reasonable care is taken to prevent dust getting into the engine during overhaul periods, and if the operating conditions are carefully observed, it is not difficult to obtain reproducible results both during check runs in a given laboratory and also between one laboratory and another. In this test an oil which gives ring stick in 480 hours with a change of oil every 120 hours, is definitely rejected. Oils which do not lead to stuck rings can be graded in order of merit in terms of carbon deposits behind the rings, lacquer on the piston skirt, sludge in the scraper ring slots, and sludge on the wire wound Purolator oil-filter, etc. Such gradings are not, however, linear in terms of the real performance value of the oil and very little difference can be detected by the Caterpillar L-1 test between a number of the best H.D. products, all of which give remarkably clean pistons after the standard test.

There may be no need, at present, for an oil to have a detergency value better than is required to give a clean piston skirt and free rings by the L-1 procedure, but developments in supercharged high-speed diesel engines, and the continued efforts of engine builders to obtain more power from an engine of a given weight and size, make it imperative to be able to grade the best types of H.D. oil more definitely, and some modification to the test is also called for to provide a more suitable technique for research purposes in relation to possible forward requirements. It is probable that a satisfactory method, which will show much greater differences between the best types of detergent oil, will be provided by a supercharged Caterpillar engine test at present being examined in the U.S.

The best of the H.D. oils not only have good detergent properties, but they lead to a marked reduction in cylinder liner and piston-ring wear in the laboratory test. It is unlikely that the whole of this improvement is obtained in service where an engine has many more starts and often runs at light load; nevertheless, the wear factor is an important consideration and service data confirm that the laboratory engine test result is not without significance. Table I gives the approximate measured liner wear figures for a series of Caterpillar tests. Piston-ring weight losses, the iron content of the used lubricating oil, and other details obtained from the tests are also included, together with laboratory examinations of the lubricating oils concerned.

Inspection of Table I shows at once how little meaning there is in the laboratory figures. The Ramsbottom carbon residue test either on the unused oil, on the same oil after D.T.D. oxidation test, or the difference between these, bear no relation to ring stick, ring-groove deposits, land deposits, the oil sludge, or the asphaltenes in the used oil; neither has the neutralization number any value in terms of the observed engine data. The only figures of importance are the iron determinations on the used oil which reflect the wear of liner and piston-rings and show how the rate of wear changes from one 120-hour period to the next. Wear becomes pronounced as soon as the operation of the rings becomes sluggish, and observation of the iron contents enables a test to be terminated when liner and ring wear become excessive.

TABLE I.

Results of Caterpillar—L.1 Test and Analytical Data.

Oil tested.	1.		2.		3.		4.		5.	
	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).
Sp. gr. at 60° F	0·9015	0·902	0·8975	0·8990	0·894	0·8975	0·8865	0·8885	0·8955	0·896
Viscosity, kin. at 140° F, c.s.	36·34	34·18	38·79	39·12	39·73	39·37	41·93	41·02	38·95	37·28
Viscosity index	66	—	87	—	74	—	96	—	76	—
Viscosity ratio (DTD oxidation test)	1·43	—	2·29	—	2·14	—	1·57	—	1·62	—
Carbon residue (Rams), %	0·26	0·46	0·55	0·77	0·46	0·75	0·48	0·72	0·12	0·38
Carbon residue (Conr), increase (DTD oxidation test)	0·88	—	1·87	—	1·44	—	1·07	—	1·10	—
Asphaltenes, %	—	0·07	—	0·10	—	0·29	—	0·22	—	0·30
Iron content.										
New oil, %	0·0005	—	0·0004	—	0·0006	—	0·0005	—	Nil	—
After 1st 120 hr, %	—	0·0067	—	0·008	—	0·0036	—	0·010	—	0·017
„ 2nd „ %	—	0·0069	—	0·009	—	0·0038	—	0·010	—	0·016
„ 3rd „ %	—	0·0065	—	0·007	—	0·0037	—	0·025	—	0·036
„ 4th „ %	—	0·0059	—	0·006	—	0·0036	—	0·027	—	0·059
Demerits.										
Ring stick	0		0		0		0		2·0	
Piston skirt lacquer deposits	0·1		0		0		0		3·0	
Ring groove deposits	1·5		0·4		1·9		2·3		3·6	
Ring land deposits	0·7		0·2		0·3		1·4		2·0	
Oil system sludge deposits	1·8		0·5		0·6		0·6		6·0	
Oil ring slots and holes deposits	0·1		0·1		0·1		0·1		2·0	
Cylinder liner wear	0·5		0·4		0·1		2·2		3·5	
Top ring wear	0·9		0·8		0·5		2·9		4·0	
Approx. liner wear after 480 hr, in.	0·0004		0·0004		0·0002		0·0024		0·0046	

(*a*) Unused oil analyses. (*b*) Used oil analyses.

Bearing Corrosion Tests.

During recent years attention has been focused on bearing corrosion, as well as on engine deposits, largely because of the trend in design towards continuously high power output from engines of limited dimensions working under extreme conditions. In these circumstances white metal bearings are often unsuitable for connecting-rod big-ends, and in the most extreme examples they may be unsatisfactory for main bearings as well. Various alternatives are in use, each with its own disadvantages, and include copper–lead, cadmium–nickel, and similar mixtures. These, although suitable on hardened crankshafts for high temperatures and high pressures, are susceptible to corrosion which may lead to consequences just as serious as those which follow the use of white metal in similar circumstances. One of the first requirements for a heavy duty oil, therefore, is that it shall not corrode copper–lead or similar bearing materials when used under extreme conditions for an acceptable length of time in service.

Probably the most widely used of the engine bearing corrosion tests is the C.R.C. L-4-545 procedure run in the Chevrolet engine.

In this test the Chevrolet 6-cyl engine is run at 3150 r.p.m. and 30 h.p. (a little more than one-third full load) for a total operating time, exclusive of the break-in run, of 36 hours, and the lubricating oil temperature in the sump is held to 280° F for S.A.E. 30 and S.A.E. 50 grade oils. Oil samples are taken at 8-hour intervals for laboratory examination, and two special pairs of copper–lead big-end bearing shells are weighed to determine loss by corrosion. Although many laboratory examinations of a comprehensive nature have been made, results from a very large number of tests confirm that they bear little useful relation to the break-down of the oil as determined by the bearing weight losses. Table II gives a series of Chevrolet results showing changes in neutralization number, asphaltenes, alteration to viscosity, and bearing weight loss, each figure being the mean of two separate engine tests. It will be obvious from study of these figures and the accompanying laboratory data that the latter are useless as a guide either to the incidence of bearing corrosion or piston varnish.

Perhaps the most valuable purpose served by laboratory tests of used engine lubricating oils is that they indicate whether the engines were running under reasonable good conditions as regards freedom from blow-by and dilution.

Tests on a wide range of oils, including normal, premium, and H.D. types, made in two different Chevrolet engines in one laboratory, gave bearing weight losses due to corrosion of the copper–lead connecting-rod bearings varying from about 0·03 to 3·1 g in the standard test of 36 hours duration.

The reproducibility of the Chevrolet test results on a given oil is good when the circumstances of the tests are considered in detail, for it must be remembered that not only were two engines used, but that the bearing specimens might be on any of three pairs of crankpins on either engine. One oil of a very stable type gave weight losses of 0·029 and 0·035 g in the two different engines; reference oil REO/7/45 gave values of 0·063 and 0·131 in engine No. 1 and 0·100 in engine No. 2; among the more corrosive oils values of 0·748 and 0·833 were obtained from the two engines on one

TABLE II.

Results of Chevrolet Bearing Corrosion Tests and Analytical Data.

Oil no.	Time to 0·1 g bearing wt. loss, hr.	Neut no unused oil, mg/KOH/g.	Neut no after 32 hr, mg/KOH/g.	Asphaltenes after 32 hr, %.	Viscosity at 140° F, c.s.		Ratio $\frac{b}{a}$	Viscosity ratio, A.M.D.T.D. oxidation test.	Carbon Res increase, A.M.D.T.D. oxidation test.	36 hr. C.R.C.–L.4 test piston lacquer demerits.
					(*a*) Unused oil.	(*b*) After 32 hr.				
6	54	0·30	1·15	0·07	41·96	46·40	1·10	1·79	1·72	0
7	52	0·4	0·70	0·07	37·88	39·02	1·03	1·15	0·29	2
8	33	Nil	1·90	0·63	39·73	47·55	1·20	2·14	1·44	1
9	23	0·05	4·10	0·76	37·67	51·75	1·37	1·15	0·33	—
10	19	0·07	3·65	2·04	36·70	54·91	1·49	1·43	0·88	4
11	11	0·03	4·15	0·90	37·87	53·32	1·41	1·14	0·21	1–2
12	11	Nil	1·65	0·15	37·77	42·80	1·13	1·37	0·83	1

sample, while reference oil REO/8/45 gave 0·678 and 0·864 on two tests on engine No. 1 and 0·723 on a test on engine No. 2. At times the results of a pair of tests were spread more than is indicated by these typical figures, but in such cases it has been found, up to the present, that a third run gives a value much nearer to the lower figure, and sometimes even below it, so that when it is impossible to make more than two runs the lower weight loss only is considered if the spread should be abnormal. Stray results may be expected from about one test in twenty.

The earlier of the oils to be engine tested were examined in the laboratory by the Sunbury Beaker Corrosion test,[1] using lead specimens with the oils heated to 160° C. The break-down times at which each oil reached the end of its induction period, and began to give a marked rise in corrosion, did not correlate in any way with engine results, but a second series of tests made with the oil held at 140° C looked more promising and at least served to segregate the very poor from the very good qualities. It was found later that better correlation was obtained when cadmium specimens were used at 160° C in the Beaker test, but even these did not give sufficient agreement with engine tests to serve either as a final guide to refining treatment, or for selection between alternative types of additive.

Tests made on a version of the Wood River Corrosion apparatus [2] were also disappointing, and the engine test still remains the only method suitable for grading except for a very rough classification.

In the Sunbury Beaker Corrosion test the oil to be examined is contained in a 1½-litre tall-form beaker closed by means of an aluminium cover. The sample is heated and stirred in the presence of a copper catalyst by means of a rectangular test-piece mounted on a rotating spindle. The test-piece and catalyst are replaced by clean specimens at regular intervals and the test-pieces washed and weighed.

Corrosivity of the oil is measured by means of the cumulative loss of the specimen test-piece over a specified period or by the extrapolated break-down time obtained from a cumulative weight loss–time curve.

In the case of the Shell Wood River Corrosion and Stability test, the oil under examination is heated in a beaker containing a flat stationary piece of bearing metal against which is pressed a rotating felt pad. The apparatus is arranged so that the rotating pad subjects the bearing metal to a constant wiping action and also renews the oil film on its surface, thus simulating the action in a journal bearing.

The test conditions, including oil temperature, loading on the pad, ventilation of the beaker, preparation of the bearing metal, etc, are closely controlled.

If a Beaker Corrosion test is carried out in such a way that the weight losses of a series of specimens can be plotted against time as the test proceeds, graphs are obtained of the types shown in Figs. 1 and 2. In each case there is an induction period during which relatively little weight loss occurs, and this is followed by a sharp break in the slope of the curve which then rises steeply. Corrosion may continue to increase in rate until the end of the test, although in a few instances the curve flattens out again in a manner suggesting the break-down products in the oil may themselves inhibit further oxidation.

In view of the nature of these break-down graphs it was decided to make

a series of runs in the Chevrolet engines with the procedure modified to allow of the copper–lead bearings being weighed after the 6-hour break-in run and then at 8-hour intervals during a run made under standard conditions of test and continued either to a bearing weight loss of between 0·5 and 1·0 g or 80 hours, whichever came first. Fig. 3 is typical of the results of tests of this sort, and it will be seen that the curves are similar to those

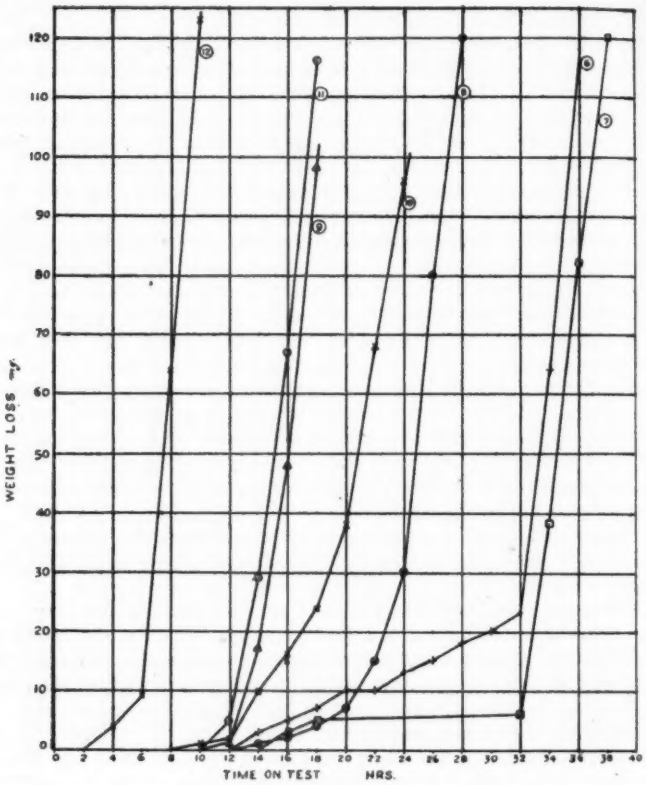


FIG. 1.

BEAKER CORROSION TESTS.

obtained from the Beaker test, insofar as each shows an induction period before serious corrosion sets in. It should be added that the bearing weight losses obtained in the normal 36-hour test are about two-thirds of those generally occurring during 36 hours from the end of the break-in period in a broken run, in which the bearings are cleaned and weighed at 8-hour intervals. This discrepancy is probably due to the cleaning process removing protective lacquer or compounds provided by the additives and thus accelerating weight losses.

It is important in engine practice to know when an additive type oil needs to be changed. It has been stated that a chemical examination to determine the more important elements of an additive remaining in a filtered sample of used oil will indicate the amount of active material still available,[3] but it is already well known that certain types of detergent additives in common use are colloids and are, therefore, capable of being removed by

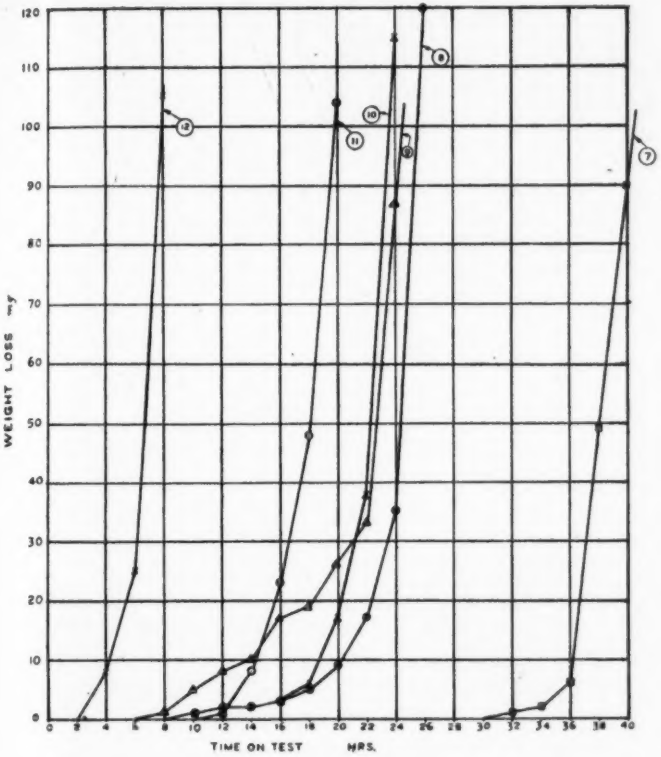


FIG. 2.

BEAKER CORROSION TESTS.

filtration while still in an active state. To overcome this difficulty a method has been developed using a centrifuge instead of filtration to remove the insolubles and spent additive from the used oil.

To verify the results obtained using the modified analytical method it is proposed to run an engine test on selected H.D. oils in a single-cylinder diesel engine. Inspections will be made at 120-hour intervals, and at the end of each a new piston and rings will be fitted, but the crankcase oil will not be renewed. The test will be continued until two successive pistons differ appreciably in lacquer deposits, indicating that the additive is no longer

acting as a detergent. Small representative samples of the crankcase oil will also be taken at the end of each period and examined for active additive by the procedure outlined above, and it is hoped in this way that a direct correlation obtained between the engine test results and the analytical results will be obtained.

If the analytical results indicate correctly when all the detergent additive is spent, or when the concentration is too low to be of any further use, the method will be invaluable for determining when oil changes should be made under service conditions.

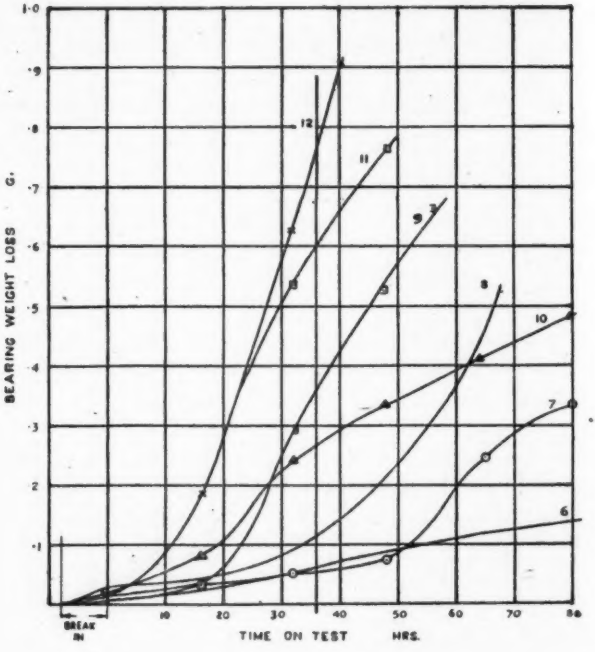


FIG. 3.

CHEVROLET BEARING CORROSION TESTS.

Less is known about the determination of active anti-corrosion compounds. Inspections of used engine oil samples taken just before the sharp rise in corrosion, and after this has reached a relatively high value have not, so far, shown any indication of important changes, and it is apparent that further research is still necessary, possibly based on progressive bearing weight loss engine tests such as those described, before a laboratory determination will be a reliable guide to the safe life of an oil in respect of its tendency to attack bearing and other metals.

Attempts have been made to grade lubricants numerically in respect of bearing corrosion in terms of bearing weight losses at the end of the 36-hour

TABLE III.

Results of Chevrolet Bearing Corrosion Tests and Beaker Corrosion Tests.

Oil no.	Loss in wt. of bearing after 36 hr, g.	Time to 0·1 g bearing wt loss, hr.	Beaker corrosion tests, Cd at 160° C.										E.B.T., hr.
			Hr to 50 mg loss.			Hr to 10 mg loss.			Hr to 5 mg loss.			Hr to actual breakdown.			
			(*a*).	(*b*).	Mean.	(*a*).	(*b*).	Mean.	(*a*).	(*b*).	Mean.	(*a*).	(*b*).	Mean.	
6	0·061	54	33	—	33	22	—	22	16	—	16	32	—	32	32–35
7	0·055	52	34	38	36	32	36	34	18	35½	27	32	36	34	35
8	0·115	33	25	24	24½	21	20	20½	19	18	18½	20	20	20	25
9	0·355	23	16	23	19½	13	14	13½	12½	10	11½	12	14	13	20
10	0·265	19	21	22	21½	14	19	16½	12½	17	14½	12	18	15	23½
11	0·690	11	15	18	16½	12½	14½	13½	12	13	12½	12	12	12	15½
12	0·760	11	7½	7	7½	6	4	5	4½	3	3¾	6	2	4	8

test period, but it is obvious that readings of this sort can be misleading. Table III gives a comparison between bearing weight losses at the end of 36 hours running; running time to a weight loss of 0·1 g; times for 50 mg and 5 mg weight loss; and times to sudden increase in rate of loss in the Beaker Corrosion test for the seven oils shown in Figs. 1 to 3.

The examples have not been specially selected, but the ratings of oils 8, 9, and 10 are sufficiently different by the various methods of test to emphasize the danger of basing conclusions on anything but properly interpreted engine data. Subsequent tests on other oils considerably increased the lack of correlation.

The true function of an engine test, when it is used for specification purposes, is to pass good oils and reject bad ones, and the continuous Chevrolet 36-hour method meets this requirement for H.D. oils when the average bearing corrosion of a pair of bearing shells does not exceed 0·10 g for acceptable grades.

For research and development it is often important not only to know whether the oil meets a given specification in relation to bearing corrosion but also what position it occupies amongst a number of other acceptable oils. The real criterion for such grading must be the number of hours for which an oil can be used under the test conditions before the bearing weight loss reaches the specified figure, and it is suggested that more consideration should be given to this type of test when valid relative ratings are needed for a series of oils, all in a given specification range.

Tests made on a time basis give a useful grading, even for oils much inferior to the acceptable minimum. The results directly indicate the reduction in running time necessary if full H.D. types are not used. For example, Oil No. 8 is an acceptable H.D. grade and suitable for, say, 2000 miles running without oil change. Oil No. 12 is not satisfactory as an H.D. grade from the corrosion point of view if it is run for an equal length of time, but it would give results in no way inferior as regards bearing weight loss if it were changed three times as frequently.

This statement assumes that the running conditions in service are such that the oil change time for the H.D. oil coincides with the onset of appreciable bearing corrosion. In practice an oil change may often be called for rather because of the need to keep down accumulations of combustion products, sludge, and abrasive material rubbed from the engine and entering through crankcase breathers, etc.

Among other specification engine tests, the L-5-545 procedure also includes examination of copper–lead bearing weight loss. In this test the crankcase oil temperature is maintained at 235° F, and the length of run is 500 hours without oil change. Present indications are that the Chevrolet run produces similar corrosion in about one-tenth of the time, and that an oil which will pass a 36-hour Chevrolet test with a bearing weight loss of not more than 0·10 g per whole bearing will also meet the L-5-545 500-hour test satisfactorily as regards corrosion.

To investigate the possibility of predicting the degree of copper–lead bearing corrosion taking place at any time during a run, without necessitating dismantling and weighing the bearing, samples of the used lubricating oil were taken at 8-hourly intervals during two standard Chevrolet L-4 tests and examined for copper. The oils selected for this purpose were oils

Nos. 6 and 11 (Tables II and III), and the results obtained are given in Table IV.

TABLE IV.

Oil no.	Copper content of used lubricating oil, per cent.			
	Sample taken after 8 hr.	Sample taken after 16 hr.	Sample taken after 24 hr.	Sample taken after 36 hr.
6	0·005	0·005	0·004	0·004
11	0·007	0·013	0·016	0·021

Although the poorer quality oil shows a progressive increase in the copper content throughout the test and the better quality oil remains at a constant low value, the results do not correlate with the weight loss curves shown in Fig. 3. This may be due to most of the copper in the used oil being present either in a metallic form, or as an insoluble compound, so that part of it settles out with the sludge at the bottom of the sump. The fact that the copper is in suspension and not in solution has been established by filtering and centrifuging the sample taken after 16 hours during the test on oil No. 11, and this reduced the copper content of the clear oil to 0·0027 per cent.

A more satisfactory procedure would probably be to obtain the lead increase in a used oil as a guide to corrosion, but this was not practicable during the work on the Chevrolet engines due to the use of leaded fuel. This method might, however, prove satisfactory for such engines as the G.M. 71 series.

Although considerable attention has been directed to the subject of bearing corrosion, it is not suggested that the most important property of an engine lubricating oil is its ability to run for long periods at high temperatures without attacking copper–lead or other susceptible bearing materials. In the majority of cases detergency, stability against oxidation and varnish-forming tendencies, resistance to emulsification, and ability to reduce wear, especially under conditions liable to induce cold corrosion, are of more importance.

The stability of an oil against varnish deposits may be determined in a preliminary manner by the standard Chevrolet test, but it is desirable also to make engine tests with lower oil temperatures, such as 210 to 230° F for a period of, say, 200 hours, to deal with normal and premium grade oils which are often used for long periods without oil change under relatively easy conditions. The observations made after such tests should include bearing corrosion as well as varnish and ring groove carbon effects. Tests for emulsification need entirely different conditions, and involve running the engine at a low load and relatively low speed for a period of, say, 50 to 100 hours, with the water jacket temperature and the oil temperature kept down to, say, 100° to 120° F, to represent winter conditions of intermittent use. Corrosive wear should be examined under similar conditions.

The difficulties of engine testing of lubricating oils are not reduced by the present need for using commercial designs of engine. The Caterpillar single-

cylinder unit stands in a class by itself and was built specifically for experimental work, but the Chevrolet, the G.M. 71, and the 4-cylinder Caterpillar engines are far from ideal. Fortunately the tests in the last two types are not of great importance, once their behaviour is understood in terms of the L-1 Caterpillar and the L-4 Chevrolet results.

As regards the Chevrolet engine, operators may avoid mechanical trouble and useless running by changing the camshaft fabric timing wheel every sixth run; by fitting new main bearings every tenth run; and using a new crankshaft about every twentieth run. Re-metalling of the white metalled connecting-rods, or their replacement with spares, is needed about every three to four runs. Cylinders last for at least forty standard test runs, if proper care is taken to guard against dust during dismantling and assembly, while cylinder-heads can be used without fitting valve-seat inserts for about fifty runs if valve grinding has been carried out intelligently.

Special operating comments are not needed for the L-1 test, apart from the usual warning that no lubricating oil engine test of any description is worth making unless every precaution is taken at all stages of dismantling and assembly to prevent dirt getting into the engine and the oil system.

When making tests of lubricating oils in engines it is most important that the fuel quality should remain unchanged for long periods, as any appreciable departure from a given specification may effect the absolute values of test results. Major changes, either of diesel fuels or petrols, may alter the relative ratings of a series of oils, and especially of those containing additives. It should also be remembered that clear petrol, in contrast with leaded, aggravates varnish deposits, and is a preferable type for low-temperature runs.

Mention of reference oils has already been made in connexion with the Chevrolet bearing corrosion tests. The use of a limited number of oils of known quality in terms of engine behaviour is essential for this class of work to check reproducibility and to serve as comparison standards. Individual laboratories are usually able to provide the necessary types independently although, of course, should grading in broad groups for classification purposes be accepted, it would be necessary to have one or two minimum permissible quality reference oils for each type of test. This subject would need very careful consideration, as it would be difficult to select a single reference oil capable of giving maximum demerits in all respects for any given procedure. Therefore, one oil might be required to give the highest permissible bearing corrosion, while another might be necessary for the same test method to give the maximum acceptable lacquer or piston deposit demerit.

Conclusions.

In conclusion it is again emphasized, first, that proper engine testing of lubricating oils depends on the collection and study of data obtained from a wide range of engines running under service conditions; secondly, there is no immediate need for an extension of specification tests such as the L-series, although there may already be a demand for new tests to help in the development of oils to meet the requirements of new engines still in the experimental stage; thirdly, the engine builder can, himself, do a great deal to avoid the need for special oils.

It is, however, evident that the steady and normal changes taking place in engine design and duty from year to year will inevitably lead to a growing use of special lubricants and this paper has been written in an attempt to show the direction for a logical extension of the engine testing of lubricants. Such testing should be based on the use of a minimum number of specially designed and built engines run under a series of conditions each selected to give a general classification standard for a range of oils, and the test procedures should be devised rather to rate oils for deposits on a demerit basis than to require running to complete ring stick, or any other criterion which would, in service, be accounted an engine failure. Bearing corrosion tests, however, may be most satisfactory if run to a specified maximum weight loss.

The authors wish to thank the chairman of the Anglo-Iranian Oil Co. Ltd. for permission to publish the results of experimental work described, which was carried out in the company's Research Laboratories at Sunbury.

References.

[1] Sunbury Beaker Corrosion Test. (To be published shortly.)
[2] "Potential Service Performance of Lubricating Oils." Waters, G. W., and Larsen, E. C., *Ind. Engng Chem. Anal.*, 1943, **15**, 550.
[3] "Oil Filters and Detergent Oils." Bridgman, Aldrich, and Romans, *S.A.E. Quarterly Transactions*, Vol. 1, No. 2, April 1947.

TANK CALIBRATION.

By the TANK CALIBRATION PANEL OF STANDARDIZATION SUB-COMMITTEE No. 1—MEASUREMENT AND SAMPLING.

FOREWORD.

The work of the Oil Measurement and Sampling Standardization Sub-Committee is divided among seven Panels. Panel "A" is responsible for the presentation of standardized procedures and equipment recommended for the purpose of calibrating all types of containers used for the storage and distribution of petroleum and petroleum products.

As and when a panel completes its study of the whole or a part of the work assigned to it, the results will be published in the form of a recommended practice in one of the Institute's publications. Thus, Panel "F" compiled and published in 1945, under the ægis of the Institute, "Tables for Measurement of Oil." Panel "B" prepared a tentative standard method for measurement of oil volumes which was published under the title "Measurement of Oil Depths" (*J. Inst. Petrol.*, 1945, **31**, 40–72).

The first part of the work of the Tank Calibration Panel has been completed and covers the calibration of oil storage tanks by the "tank strapping" and "internal diameter" methods. The results are given in the form of a tentative standard method.

In presenting its recommendations on the tank strapping method, the Panel took full cognizance of the work done by the American authorities, particularly that of the American Petroleum Institute, covered by its Code No. 25.

Panel "A" makes clear the following point in the text of its document, and this has the full support of Standardization Sub-committee No. 1.

> "Nothing in this method shall require the recalibration of any tank merely because methods previously used in calibration are not entirely in accordance with those now laid down. The method shall, however, be applied in full whenever calibration or recalibration by external strapping or internal measurement is undertaken."

The procedures outlined are offered for comment and criticism, which will be warmly welcomed. The views of those with experience in this sphere of activity will enable the Panel so to amend the tentative method that it can later be put forward with full support as an I.P. Standard Method.

The membership of Panel "A" responsible for this document, is as follows :—

F. Tipler (*Chairman*) (Anglo-American Oil Co. Ltd.).
W. L. Coats (Shell-Mex & B.P. Ltd.).
F. Gill (Anglo-Iranian Oil Co. Ltd.).
A. W. Higson (National Benzole Co. Ltd.).
W. F. Jelffs (B. & R. Redwood).
J. R. Lewis (Shell Petroleum Co. Ltd.).
E. Stokoe ("Shell" Refining & Marketing Co. Ltd.).
E. G. V. Williams (B. & R. Redwood).
G. M. Williamson (Anglo-Iranian Oil Co. Ltd.).

The specifications for the apparatus included in the Appendices were prepared by Panel "G."

H. HYAMS.
Chairman, Standardization Sub-committee No. 1.

TANK STRAPPING.

1. (*a*) A tank is "strapped" when its external circumferences are measured for later preparation of a table of capacities; the work involves measurement of :—

(i) An adequate number of these circumferences, with their approximate position on the tank. If during measurement the tape is displaced from the tank surface, measurements must be suitably corrected.

(ii) The thicknesses of the tank plates, with any other data needed for proper calculation of internal circumferences from the external circumferences measured.

(iii) The volumes of any deadwood, that is, of any fitting or other object which adds to or subtracts from the space available for oil, with the levels affected.

(*b*) Tanks are recalibrated infrequently and a table once prepared may be kept in use over several years. Adequate care should therefore be taken to prevent the occurrence of undetected mistakes at any point of the process.

(*c*) When drawings for the tanks are available, the strappings and other measurements should be compared with those obtainable from the drawings, and any measurements which show substantial discrepancies on this comparison should be verified. A similar process of check should be employed in all cases in which reliable information beyond the measurements taken is available.

(*d*) Expressed as a percentage on the total capacity of the tank, the uncertainties in the tables resulting from strapping are the greater the smaller the tank diameter.

(*e*) Nothing in this method shall require the recalibration of any tank merely because methods previously used in calibration are not entirely in accordance with those now laid down. The method shall, however, be applied in full whenever calibration or recalibration by external strapping is undertaken.

(*f*) The method described below is intended to be applied to tanks whose courses are vertical cylinders or nearly so.

(*g*) Corrections not specifically mentioned in the method shall not be applied in the calculation of tables.

(*h*) The methods given below shall not be applied to abnormally distorted tanks.

2. *Circumference Measurements.*

(*a*) Circumferences shall be measured after the tank has been subjected to a full water test, and shall in general be measured when the tank is 80 per cent full.

(*b*) Circumferences shall be taken with steel tapes which meet the Institute of Petroleum Specification No. A.1, attached.

(*c*) Circumferences shall be measured in a plane at right angles to the axis of the tank at the following levels, this involving three strappings per course :—

(i) 4 to 6 in above the level of the top of the bottom angle iron of the tank.

(ii) 4 to 6 in above the upper edge of each horizontal overlap between courses.

(iii) 4 to 6 in below the lower edge of each horizontal overlap between courses.

(iv) 4 to 6 in below the level of the lowest part of the top angle iron of the tank.

(v) At the middle position of each course.

(*d*) If for any reason it is impracticable, even with the use of the step-over (see para (*j*)), to take a strapping at the normal level, then a strapping shall be taken as close to this level as practicable, but not nearer the angle iron or seam. The strapper's notes shall give the level at which this circumference has been measured, with an explanation why the normal level had to be deserted.

(*e*) If the tape is not in close contact with the surface of the tank throughout its whole path, the step-over shall be applied so that a correction may be calculated adjusting the gross circumference for this effect.

(*f*) The tank may be strapped by using either of the methods described below.

(i) If a tape not long enough to encircle the tank completely is to be used, then after the level of the tape path has been chosen, fine lines shall be scribed perpendicular to this path, these allowing the circumference to be measured in sections. The scribed lines may only be drawn in the middle third of any plate. In this case a tension of 10 lb shall be applied to the tape while each section is being measured. Subject to (*e*) above, the external circumference of the tank is then the sum of the lengths between the scribed lines.

The vertical lines shall be inscribed at such distances as will ensure that the whole of the length of the tape used is under the observations of one or other of the calibrators.

(ii) If a tape long enough to encircle the tank completely is to be used, then either

(*a*) A circumference is measured at some convenient height on one of the lower courses of the tank, this in sections as in (i), the lengths of these sections being added together without application of any correction whatever. The long tape is then applied to the same circumference, the tension on it being increased until the circumference obtained from its readings is the same as that just determined.

The tension at which this occurs is read off on the spring gauges through which the long tape has been held, and in measuring other circumferences on the same tank, the tension so read off is to be applied when the new circumference readings are being taken.

In this process the long tape shall be so held that its ends pass each other within the middle third of any plate, with the scale on the one end as near as practicable to the scale on the other, so that the reading taken is that on the part of the tape which has passed round the tank, against the 1-ft graduation on the other end. The circumference measured is then 1 foot less than the reading so shown; or

(*b*) The long tape may be brought into position for measurement of the circumference in question, the ends crossed as described in (*a*) and a tension of 10 ± 1 lb applied through a spring gauge to each end. This tension is maintained, while an assistant passes

round the tank raising the tape in sections a little from the tank surface, so that the tension of 10 lb is known to be transmitted around the tank. This occurs when further raising of the tape does not alter the reading obtained opposite the 1-ft graduation, as described in (*a*).

(g) *Repetition of Measurement.*

After a circumference has been measured, the tape may be shifted a little around the tank, brought to level and tension as above, and the reading repeated. The mean of these two circumferences shall be taken as the tank circumference for subsequent calculation.

(h) *Tolerances.*

Circumference measurements shall be considered satisfactory if repetition as in (*g*) above shows agreement with the following tolerances :—

Circumference in feet.	Tolerance.	
	In feet.	In inches.
100	0·03	$\frac{3}{8}$
101–200	0·04	$\frac{1}{2}$
201–300	0·05	$\frac{5}{8}$
301 and over . . .	0·06	$\frac{3}{4}$

The tolerance on circumferences below 100 ft shall be a proportional part of 0·03 ft or of $\frac{3}{8}$ in.

(j) *Step-overs.*

These are frames holding two scribing points rigidly, so that these can conveniently be applied to the tape path on either side of any obstruction or distortion in the way of the tape. The step-over is to be used whenever the tape leaves the tank surface as the result of an obstruction in its path, or of some distortion of the tank plates or seams.

When needed to correct for tape displacement at vertical seams without butt-straps, an average correction may be determined, this, multiplied by the number of vertical seams per course, giving the correction to be applied.

No correction need be made if its omission does not lead to error exceeding 0·02 per cent of the open capacity of the tank.

The gap between the scribing points must be sufficient to allow them to be applied well clear of any local distortion, and the frame itself must be so constructed that it does not touch the tank when the scribing points are applied to the tape path. Rigidity of construction is essential; suitable designs are illustrated in the attached Appendix I.

The strapping tape shall be stretched as if in measurement of any accessible circumference on the tank which is being calibrated, but not within a foot of any horizontal seam. The scribing points shall then be applied to the tape near the middle of a plate where the tape is fully in contact with the tank surface. The length between the points, as measured on the curved tape, is then read off as closely as possible, fractions of tape divisions being estimated. The readings shall be repeated on four plates

equally spaced around the circumference, and the average of the results taken as the step-over interval for the tank concerned. The readings for any one step-over will vary with the tank diameter, since they are made on surfaces differently curved.

The use of the step-over corrects circumferences for the effect on them of vertical seam overlaps, but it does not correct the tank tables for the effect as deadwood of internal projection of the seam edges.

With the tape still in position and under the tension used in strapping, the step-over shall be applied to the tape on either side of any obstruction or distortion lying on the tape path, and a reading taken of the length of tape included between the scribing points. The excess of this length over the step-over interval shall be subtracted from the circumference figure obtained on strapping, and the result shall be taken as the corrected circumference, free from error due to the displacement of the tape from its proper path by the obstruction concerned. If, as may occur with distortions, the step-over interval is greater than the tape reading across the distortion, then the excess shall be added to, not subtracted from, the uncorrected circumference.

3. *Measurements on Plates.*

(*a*) The thickness of the plates of each course shall be measured at not less than four places per course, these being chosen to avoid caulked parts of the seams. If no places are free from visible effects of caulking, then the best possible estimate of the plate thickness should be made. In all cases where this is possible, the measurements of the plate thicknesses shall be compared with those given on the makers' drawings, and any serious discrepancy between these and the actual measurements shall be verified. If the tank has been painted, the paths of the tape round each course shall be inspected, and any lumps of paint removed before circumferences are measured.

(*b*) It shall be permissible to measure the thickness of the paint, if any, on the tank, by flaking off small pieces from the tape paths and holding these edgewise against a steel rule graduated in 64ths of an inch. The thickness of the paint so determined shall be added to the corresponding plate thickness in subsequent calculations.

(*c*) When circumstances permit, the heights of the courses shall be measured internally as follows: At such a part of the tank as will allow the tape to lie close to the tank sides, a dip-tape and weight to the specifications in the Appendix to the Institute of Petroleum Standard Method for Measurement of Oil Depths are suspended in such a way that the dip-weight just touches the tank bottom beside the bottom angle iron. The vertical heights corresponding to each internal plate edge, and to the upper side of the top angle iron are then read off the tape, this to the nearest inch. The effective height of each course is then the difference between the two consecutive readings which include the course.

(*d*) When it is impracticable to measure the course heights internally, then they shall be measured externally, due allowance being made for the effect of horizontal seam overlaps. The heights obtained shall be the vertical distances to the nearest inch between successive edges of the courses as exposed internally in the tank.

(*e*) It shall be permissible to measure these heights at more than one vertical around the tank, and to average the results so obtained.

4. *Welded Tanks.*

The following modification to the method shall be applied when welded tanks are to be calibrated :—

(a) *Plate Thicknesses.*

If the plates are lap-welded, then thicknesses shall be measured. If any course is butt-welded so that the plate thicknesses cannot be measured after erection, it shall preferably be measured before erection; but, if this procedure is also impossible, the corresponding plate thickness shall be taken from the tank drawing.

(b) *Levels Strapped.*

If the plates are lap-welded or butt-welded, three strappings shall be taken on each course as described in Section 2 (*c*), (i) to (v), but the 4- to 6-in distance specified in paragraphs 2 (*c*), (i) to (iv) shall be increased to 11 to 13 in.

5. *Deadwood:*

(*a*) The principle to be followed in measuring up deadwood is that records should permit (1) adequate allowance for the volumes of oil displaced or admitted by the tank fitting, and (2) adequate allocation of these effects to the levels affected in the tank.

(*b*) Such measurements as are necessary for the calculation of the volume of each piece of deadwood shall be taken.

(*c*) In general, it is sufficient to measure the heights above the underside of the bottom angle iron of the lowest and highest levels at which the deadwood begins to affect the capacity of the tank, but where the effect of the deadwood is large, and when its shape is irregular, then the deadwood should be measured in such sections as will sufficiently allow for its varying effect on the tank capacity at various heights.

(*d*) The measurements of the dimensions of any particular piece of deadwood shall be so taken as to allow calculation of the volume of the deadwood correct to the nearest Imperial gallon. Measurements of the levels affected by the deadwood shall be so taken that the error in the tables at any level, as compared with strict geometrical calculation, shall not exceed five Imperial gallons. Deadwood of irregular shape shall be so measured that this condition can be met.

(*e*) It shall be allowable to include as deadwood in the calculation of the tank table any feature which in fact affects the tank's capacity for oil, but it shall be permissible to neglect any deadwood provided that (1) this neglect does not lead to error exceeding 0·02 per cent of the open capacity of the tank, and (2) the deadwood so neglected is distributed evenly, or substantially so, over the whole height of the tank.

(f) *Tank Bottoms.*

(i) When the tank bottom is substantially horizontal, *e.g.*, when the tank is carried on a level concrete raft or steel structure, then no allowance shall be made for bottom irregularities.

(ii) When the tank bottom is not horizontal, but those levels so affected are not used in calculating quantities put into or taken out of the tank, then the tank table may be calculated as if the bottom were horizontal, but no capacities shall be shown in the table below the highest level at which the bottom irregularities affect the tank capacity.

(iii) It shall be permissible to calibrate the tank bottom by measuring in known and suitable volumes of water, depths being measured after each addition, the tank tables for these levels being constructed from these measurements on sound mathematical principles.

The highest level and capacity shown in the water-calibration table so made shall then be the datum level and capacity, from which is to be constructed the rest of the table by calculation as described in Section 7 below.

6. *Floating Roof Tanks.*

(a) *Definitions :*

(i) The roof is " at rest " when it is supported by members resting on the tank bottom, with the liquid surface below and out of contact with any part of the roof plates.

(ii) It is " oil-borne " when its members are all held clear of the tank bottom by the buoyant effect of the oil in the tank.

(iii) It is " partly-immersed " between conditions (i) and (ii).

(iv) Level " A "—a level not less than $1\frac{1}{2}$ in nor more than $2\frac{1}{2}$ in below the lowest point of the roof plates when the roof is " at rest."

(v) Level " B "—a level not less than $1\frac{1}{2}$ in nor more than $2\frac{1}{2}$ in above the free oil surface when the roof is in its lowest oil-borne position.

(b) *Tank Shell Measurements.*

The tank shall be strapped and other calibration measurements made exactly as for tanks with fixed roofs. These measurements may include water calibration of the tank bottom with the roof at rest, as described in Section 4 (*f*).

(c) *Determination of Levels " A " and " B."*

(i) The level corresponding to the lowest part of the roof plates shall be measured and level " A " shall be the level, to the nearest inch, not less than $1\frac{1}{2}$ in nor more than $2\frac{1}{2}$ in below the level so measured.

(ii) With the roof resting fully on its supports, four short horizontal white lines about 1 in wide are painted on the tank sides, so placed that viewed from some definite point their lower edges are just above four similar lines marked on the roof edges or shoes. Oil is then slowly pumped into the tank; when all roof-markings are seen to have moved upwards, dips are taken and the roof regarded as oil-borne. From some chosen viewpoint on the dipping platform, a similar process may be used, the position of the roof being noted against rivet-heads on vertical seams, or other markings on the tank walls, instead of painted marks. In both cases the points of reference must extend around the greater part of the tank interior, and movement relative to all points

of reference must be seen. Level " B " shall be the level, to the nearest inch, not less than 1½ in nor more than 2½ in above the level so measured.

(d) *Deadwood.*

(i) Fixed deadwood shall be measured and allowance made as described in Section 4.

(ii) The floating roof supports, drain line, and other accessories below the roof shall be treated as fixed deadwood in the position they occupy when the roof is " at rest."

(iii) The quantity of oil displaced by the roof when floating shall be considered as deadwood and when preparing the tank table the total allowance to be made shall be distributed, according to the shape of the roof, between the level at which the oil just reaches the lowest point of the roof and the level at which the roof just becomes oil-borne. To determine the total allowance to be made, the weight of the roof and any attachments not treated as fixed deadwood shall be calculated from the dimensions of the component parts, taking the weight of a cubic foot of steel as 496 lb. The weight so obtained, converted to units of volume or capacity of the quality of oil in the tank, is the total allowance to be made in the table. The manner in which this total allowance is to be distributed over the parts of the tank table affected can most accurately be made by admitting known quantities of oil into the tank and recording the corresponding oil levels at close intervals over the oil depths concerned. If this calibration method is not practicable the distribution may be computed from field measurements of the shape of the roof, preferably made with the aid of a surveyor's level.

(e) *Computation, Form, and Use of Tables for Floating Roof Tanks.*

(i) Except as modified below, tables shall be prepared in accordance with Sections 7 and 8.

(ii) Allowance for deadwood shall be made as described in Subsection 6 (*d*).

(iii) That part of the table between level " A " and level " B " shall be marked " Not Accurate," and the oil surface should not be carried into or through this portion of the tank if accurate accounting is desired. Most accurate results will be obtained if measurements before and after an oil movement are both taken while the roof is oil-borne.

(iv) The specific gravity of the oil for which the roof displacement has been calculated shall be recorded on the tank table. If the tank is to be used for oils of varying specific gravity ranges, a table may be appended giving allowances to be added to or subtracted from the oil volumes or capacities according to the specific gravity of the oil. This additional table shall only be used when the roof is oil-borne. To avoid confusion, separate tables should be issued for certain wide changes in commodity, as, for example, heavy crude, light crude, straight gasoline, and casing-head gasoline, with the gravity range clearly indicated on the face of each such supplementary table.

(v) When measurements are taken before and after an oil movement, correction need not be made for differences between the specific

gravity of the oil and the specific gravity used in computing the table, provided both measurements are taken with the roof oil-borne. The correction only affects the deadwood distributed over that part of the tank table marked " not accurate " and need therefore only be applied if careful stock measurements are required, or if one of the two sets of measurements must be taken below the oil-borne position.

(vi) It is considered impracticable to allow in the tank table for the effects of —

(*a*) Rain-water retained by the roof,
(*b*) Varying friction of the roof shoes, and
(*c*) Varying immersion of roof supports.

7. *Computation of Contents of Tanks.*

(*a*) The calculations shall be made on accepted geometrical principles and the recommendations set out below are for guidance. No tank table shall be regarded as invalid because greater precision has been aimed at or secured in the application of the method.

(*b*) Circumferences and plate thicknesses shall be converted to feet and decimals of a foot, to the nearest 0·001 in each case.

(*c*) As the strapping tape is calibrated at 68° F, and the tank table is to be correct in use at 60° F, from each measured circumference shall be subtracted 8/100,000ths of itself, before the figure is taken into further calculation.

(*d*) The mean external circumference of the course shall be one-third of the sum of the three circumferences as measured on each course in accordance with Section 2 (*c*).

(*e*) The mean internal circumference of the course shall then be calculated from the mean external circumference, by subtracting from the former the product of the plate thickness in feet by 6·2832. If the tank is painted, allowance for this may be made as in Section 3 (*b*).

(*f*) The open capacity of each course, that is, its capacity without allowing for deadwood, shall be calculated as if the course were a true cylinder of the mean internal circumference determined as above. This rule shall apply to vertical cylinders of in-and-out, telescopic, or shingled construction.

The open capacity of each course in Imperial gallons per inch of height shall be obtained by using the formula

$$\frac{C^2 \times 144}{4\pi \times 277{\cdot}42} \quad \text{or } 0{\cdot}0413062 \times C^2$$

where C is the mean internal circumference in feet, or by any process mathematically equivalent.

8. *Form of Tank Tables.*

Provided that tank tables have been constructed in accordance with the principles laid down in Section 7 above, the form in which the table is set out will not alter the accuracy of the figures obtained from it, but the following principles should be applied in constructing tank tables.

(*a*) The intervals of dip at which the tables are set out should not be so great that interpolation for intermediate dips is troublesome. It is convenient to set out tables at intervals of dip not greater than 2 in, for then a small proportional-parts table, calculated on the average content of the tank per unit depth, may be used for calculating the gallonages corresponding to intermediate fractional dips. Many may prefer to set the table out at 1-in intervals in dip.

Levels affected by bottom irregularities and deadwood should not be included in calculating the average capacity per unit depth used for the proportional-parts table; and this table should not be applied in interpolations at these levels.

(*b*) The table may be set out more fully; this may be justifiable in some cases where the greatest speed in calculation is desired, but it should be remembered that a table set out on a single sheet of paper is often quicker in use than one which occupies several pages.

(*c*) It should be remembered that, at best, no oil measurement can be relied on to nearer than one part in 10,000. Commercial tables should never be set out to show any fractions of an Imperial gallon, and minor discrepancies, within the limit just mentioned, should be disregarded.

(*d*) In general, therefore, it is recommended that tables should be set out to show Imperial gallons, this at intervals of 2 in or of 1 in in dip, with a proportional-parts table for intermediate dips, this latter being set out against those fractions of an inch into which the dip-tapes of the user are divided.

Internal Measurement of Tanks.

A. The internal measurement method is carried out by measuring internal diameters for later preparation of a table of capacities; the work involves measurement of:—

(i) An adequate number of these diameters with their approximate position on the tank.

(ii) The volumes of any deadwood, that is, of any fitting or other object which adds to or subtracts from the space available for oil, with the levels affected.

B. Tanks are recalibrated infrequently and a table once prepared may be kept in use over several years. Adequate care should therefore be taken to prevent the occurrence of undetected mistakes at any point of the process.

C. When drawings for the tanks are available, the diameters and other measurements should be compared with those obtainable from the drawings, and any measurements which show substantial discrepancies on this comparison should be verified. A similar process of check should be employed in all cases in which reliable information beyond the measurements taken is available.

D. In all practicable cases an external circumference should be measured at the bottom of the second course at the same height above the horizontal seam at which a set of diameters has been taken, and the results compared. If a substantial discrepancy is shown the comparison should be verified.

E. Expressed as a percentage on the total capacity of the tank, the uncer-

tainties in the tables, resulting from the measurements of diameters, are greater the smaller the tank diameter, therefore the smaller the tank diameter the greater the number of necessary measurements.

F. Nothing in this method shall require the recalibration of any tank merely because methods previously used in calibration are not entirely in accordance with those now laid down. The method shall, however, be applied in full whenever calibration or recalibration by internal measurement is undertaken.

G. The method described below is intended to be applied to tanks whose courses are vertical cylinders or nearly so.

H. Corrections not specifically mentioned in the method shall not be applied in the calculation of tables.

I. The methods given below are not to be applied to abnormally distorted tanks.

J. *Diameter Measurement.*

(*a*) Diameters shall be measured after the tank has been subjected to a full water test and when it is clean and dry.

(*b*) Diameters shall be measured with steel tapes which meet the Institute of Petroleum specification No. B.1, attached.

(*c*) The measurements shall be taken at diametrically opposite points at the following levels on each course, the minimum number allowable being three on each plate, no measurement to be taken nearer than 12 in to any vertical seam :

(i) *Riveted Tanks.*

(*a*) 6 in above the upper edge of each horizontal overlap.
(*b*) Half-way between the upper and lower edges of the plates.
(*c*) 6 in below the lower edge of each horizontal overlap.

(ii) *Lap- or Butt-Welded Tanks.*

(*a*) 12 in above the upper edge of each horizontal overlap.
(*b*) Half-way between the upper and lower edges of the plates.
(*c*) 12 in below the lower edge of each horizontal overlap.

(*d*) If for any reason it is impracticable to take measurements at the positions described above, then the diameter shall be taken as close to the proper position as practicable, but not nearer the horizontal or vertical seams. The reason for the deviation shall be recorded in the field notes.

(*e*) Measurements shall be taken with the end of the steel tape attached to a dynamometer (which meets the Institute of Petroleum specification No. B.2, attached *), one operator placing the dynamometer on the predetermined point and the second operator placing a rule (which meets the Institute of Petroleum specification No. B.3, attached) end on to a point diametrically opposite. The tape shall be pulled along the rule until 10-lb tension is registered by the sounding of the buzzer in the dynamometer. A firm grip shall be maintained on the rule and tape to prevent any alteration in their relative positions, the tension released, and a reading taken on the tape at that end of the rule which was against the side of the

* A Redwood Dynamometer is illustrated in Appendix II.

tank. The operation shall be repeated at the various positions at which measurements are required throughout the tank. The measurements shall be recorded clearly in white chalk on the steel plates in such a manner as to indicate the positions at which they were taken.

(*f*) Each measurement of diameter shall be recorded to the nearest 0·1 in.

(*g*) Repeat measurements of diameter should not differ by more than ± 0·1 in.

K. *Corrections.*

(*a*) Corrections for the effect of sag shall be applied to the average diameter of each course using the following formula :—

$$\frac{W^2S^3}{24P^2}$$

where :— P = pull on tape in lb.
S = span of tape in feet.
W = weight of tape in lb per ft.

Note 1. This can reduce to KXS^3. For a tape ½ in wide and 0·008 in thick of steel 489 lb/cu. ft., values of K to give the correction in inches will be :—

P	K
9½ lb	$5{\cdot}461 \times 10^{-6}$
10 lb	$5{\cdot}192 \times 10^{-6}$
10½ lb	$4{\cdot}942 \times 10^{-6}$

Note 2. The equation of the catenary may be used if desired, but the above formula gives practically the same results and is less cumbersome.

(*b*) Corrections for the effect of stretch are unnecessary because the tension applied is that at which the tape is standardized.

(*c*) Corrections for the length of the dynamometer when registering a pull of 10 lb shall be made to the average diameter of each course. The dynamometer length at a 10-lb pull shall be taken accurately before it is put into commission and subsequently checked before and after the calibration of each tank, the final checking being made before leaving the site.

L. *Measurements of Heights of Plates.*

When circumstances permit, the heights of the courses shall be measured internally as follows : At such a part of the tank as will allow the tape to lie close to the tank sides, a dip-tape and weight to the specifications in the Appendix to the Institute of Petroleum Standard Method for Measurement of Oil Depths are suspended in such a way that the dip-weight just touches the tank bottom beside the bottom angle iron. The vertical heights corresponding to each internal plate edge, and to the upper side of the top angle iron are then read off the tape, this to the nearest inch. The effective height of each course is then the difference between the two consecutive readings which include the course.

M. *Deadwood.*

(*a*) The principle to be followed in measuring up deadwood is that records should permit (1) adequate allowance for the volumes of oil

displaced or admitted by the tank fitting, and (2) adequate allocation of these effects to the levels affected in the tank.

(*b*) Such measurements as are necessary for the calculation of the volume of each piece of deadwood shall be taken.

(*c*) In general, it is sufficient to measure the heights above the underside of the bottom angle iron of the lowest and highest levels at which the deadwood begins to affect the capacity of the tank, but where the effect of the deadwood is large, and when its shape is irregular, then the deadwood should be measured in such sections as will sufficiently allow for its varying effect on the tank capacity at various heights.

(*d*) The measurements of the dimensions of any particular piece of deadwood shall be so taken as to allow calculation of the volume of the deadwood correct to the nearest Imperial gallon. Measurements of the levels affected by the deadwood shall be so taken that the error in the tables at any level, as compared with strict geometrical calculation, shall not exceed five Imperial gallons. Deadwood of irregular shape shall be so measured that this condition can be met.

(*e*) It shall be allowable to include as deadwood in the calculation of the tank table any feature which in fact affects the tank's capacity for oil, but it shall be permissible to neglect any deadwood provided that (1) this neglect does not lead to error exceeding 0·02 per cent of the open capacity of the tank, and (2) the deadwood so neglected is distributed evenly, or substantially so, over the whole height of the tank.

(*f*) *Tank Bottoms.*

(i) When the tank bottom is substantially horizontal, *e.g.*, when the tank is carried on a level concrete raft or steel structure, then no allowance shall be made for bottom irregularities.

(ii) When the tank bottom is not horizontal, but those levels so affected are not used in calculating quantities put into or taken out of the tank, then the tank table may be calculated as if the bottom were horizontal, but no capacities shall be shown in the table below the highest level at which the bottom irregularities affect the tank capacity.

(iii) It shall be permissible to calibrate the tank bottom by measuring in known and suitable volumes of water, depths being measured after each addition, the tank tables for these levels being constructed from these measurements on sound mathematical principles.

The highest level and capacity shown in the water-calibration table so made shall then be the datum level and capacity from which is to be constructed the rest of the table by calculation as described in Section O below.

N. *Floating Roofs.*

(*a*) *Definitions :*

(i) The roof is " at rest " when it is supported by members resting on the tank bottom, with the liquid surface below and out of contact with any part of the roof plates.

(ii) It is " oil-borne " when its members are all held clear of the tank bottom by the buoyant effect of the oil in the tank.

(iii) It is " partly-immersed " between conditions (i) and (ii).

(iv) Level " A "—a level not less than 1½ in nor more than 2½ in below the lowest point of the roof plates when the roof is " at rest."

(v) Level " B "—a level not less than 1½ in nor than 2½ in above the free-oil surface when the roof is in its lowest oil-borne position.

(b) *Tank Shell Measurements.*

The tank shall be strapped and other calibration measurements made exactly as for tanks with fixed roofs. These measurements may include water calibration of the tank bottom with the roof at rest, as described in Section M (*f*).

(c) *Determination of Levels " A " and " B."*

(i) The level corresponding to the lowest part of the roof plates shall be measured and level " A " shall be the level, to the nearest inch, not less than 1½ in nor more than 2½ in below the level so measured.

(ii) With the roof resting fully on its supports, four short horizontal white lines about 1 in wide are painted on the tank sides, so placed that viewed from some definite point their lower edges are just above four similar lines marked on the roof edges or shoes. Oil is then slowly pumped into the tank; when all roof-markings are seen to have moved upwards, dips are taken, and the roof regarded as oil-borne. From some chosen viewpoint on the dipping platform a similar process may be used, the position of the roof being noted against river-heads on vertical seams, or other markings on the tank walls, instead of painted marks. In both cases the points of reference must extend around the greater part of the tank interior, and movement relative to all points of reference must be seen. Level " B " shall be the level, to the nearest inch, not less than 1½ in nor more than 2½ in above the level so measured.

(d) *Deadwood.*

(i) Fixed deadwood shall be measured and allowance made as described in Section M.

(ii) The floating roof supports, drain line, and other accessories below the roof shall be treated as fixed deadwood in the position they occupy when the roof is " at rest."

(iii) The quantity of oil displaced by the roof when floating shall be considered as deadwood and when preparing the tank table the total allowance to be made shall be distributed, according to the shape of the roof, between the level at which the oil just reaches the lowest point of the roof and the level at which the roof just becomes oil-borne. To determine the total allowance to be made, the weight of the roof and any attachments not treated as fixed deadwood shall be calculated from the dimensions of the component parts, taking the weight of a cubic foot of steel as 496 lb. The weight so obtained, converted to units of volume or capacity of the quality of oil in the tank, is the total allowance to be made in the table. The manner in which this total allowance is to be distributed over the parts of the tank table affected

can most accurately be made by admitting known quantities of oil into the tank and recording the corresponding oil levels at close intervals over the oil depths concerned. If this calibration method is not practicable the distribution may be computed from field measurements of the shape of the roof, preferably made with the aid of a surveyor's level.

(e) *Computation, Form, and Use of Tables for Floating Roof Tanks.*

(i) Except as modified below, tables shall be prepared in accordance with Sections O and P.

(ii) Allowance for deadwood shall be made as described in Subsection N (*d*).

(iii) That part of the table between level "A" and level "B" shall be marked "Not Accurate," and the oil surface should not be carried into or through this portion of the tank if accurate accounting is desired. Most accurate results will be obtained if measurements before and after an oil movement are both taken while the roof is oil-borne.

(iv) The specific gravity of the oil for which the roof displacement has been calculated shall be recorded on the tank table. If the tank is to be used for oils of varying specific gravity ranges, a table may be appended giving allowances to be added to or subtracted from the oil volumes or capacities according to the specific gravity of the oil. This additional table shall only be used when the roof is oil-borne. To avoid confusion, separate tables should be issued for certain wide changes in commodity, as, for example, heavy crude, light crude, straight gasoline, and casing-head gasoline, with the gravity range clearly indicated on the face of each such supplementary table.

(v) When measurements are taken before and after an oil movement, correction need not be made for differences between the specific gravity of the oil and the specific gravity used in computing the table, provided both measurements are taken with the roof oil-borne. The correction only affects the deadwood distributed over that part of the tank table marked "Not Accurate" and need therefore only be applied if careful stock measurements are required, or if one of the two sets of measurements must be taken below the oil-borne position.

(vi) It is considered impracticable to allow in the tank table for the effects of:—

(*a*) Rain-water retained by the roof;
(*b*) Varying friction of the roof shoes; and
(*c*) Varying immersion of roof supports.

O. *Computation of Contents of Tanks.*

(*a*) The calculations shall be made on accepted geometrical principles and the recommendations set out below are for guidance. No tank table shall be regarded as invalid because greater precision has been aimed at or secured in the application of the method.

(*b*) The diameters as measured shall be adjusted for sag and dynamometer correction and converted to inches to the nearest 0·01 in.

(*c*) As the measuring tape is calibrated at 68° F and the tank table is to be correct in use at 60° F, from each measured diameter shall be subtracted 8/100,000ths of itself before the figure is taken into further calculation.

(*d*) The mean diameter of each course shall be the sum of all the diameters measured on that course in accordance with Section J (*c*), divided by the total number of diameters measured on that course.

(*e*) The open capacity of each course, that is, its capacity without allowing for deadwood, shall be calculated as if the course were a true cylinder of the mean internal diameter determined as above. This rule shall apply to vertical cylinders of in-and-out, telescopic, or shingled construction.

The open capacity of each course in Imperial gallons per inch of height shall be obtained using the formula

$$\frac{D^2 \times \pi}{277{\cdot}42 \times 4} \quad \text{or } 0{\cdot}00283108 \times D^2$$

where D is the mean internal diameter in inches, or by any process mathematically equivalent.

P. *Form of Tank Tables.*

Provided that tank tables have been constructed in accordance with the principles laid down in Section O above, the form in which the table is set out will not alter the accuracy of the figures obtained from it, but the following principles should be applied in constructing tank tables.

(*a*) The intervals of dip at which the tables are set out should not be so great that interpolation for intermediate dips is troublesome. It is convenient to set out tables at intervals of dip not greater than 2 in, for then a small proportional-parts table, calculated on the average content of the tank per unit depth, may be used for calculating the gallonages corresponding to intermediate fractional dips. Many may prefer to set the table out at 1-in intervals in dip.

Levels affected by bottom irregularities and deadwood should not be included in calculating the average capacity per unit depth used for the proportional-parts table; and this table should not be applied in interpolations at these levels.

(*b*) The table may be set out more fully; this may be justifiable in some cases where the greatest speed in calculation is desired, but it should be remembered that a table set out on a single sheet of paper is often quicker in use than one which occupies several pages.

(*c*) It should be remembered that at best, no oil measurements can be relied on to nearer than one part in 10,000. Commercial tables should never be set out to show any fractions of an Imperial gallon, and minor discrepancies, within the limit just mentioned, should be disregarded.

(*d*) In general, therefore, it is recommended that tables should be set out to show Imperial gallons, this at intervals of 2 in or of 1 in dip, with a proportional-parts table for intermediate dips, this latter being set out against those fractions of an inch into which the dip-tapes of the user are divided.

SPECIFICATIONS FOR TANK CALIBRATION APPARATUS.

A. *Strapping Method.*

1. *Steel Tapes.*

(a) *Material.* Carbon steel of the best quality, as currently used for measuring tapes.

(b) *Construction.* Each tape shall be fitted at its end with a swivel allowing easy attachment of the spring balance 4½ to 6 in outside the first graduation on the tape. Tape reels, cases, and any other incidental fittings not specifically mentioned in this specification may be ordered as desired.

(c) *Dimensions.* Width ¼ in or ⅜ in as desired; thickness uniform and approximately 0·01 to 0·02 in, as desired.

(d) *Graduation.*

(i) Graduation shall be on one side only of the tape.

(ii) The tape shall be graduated from the beginning of its markings at every whole foot of its length.

(iii) At least the first foot of its graduated length shall be further subdivided into either inches and tenths of inches, or tenths and hundredths of a foot.

(e) *Figuring.* The length from the zero graduation shall be clearly shown at every whole foot, with figuring at every inch or tenth of a foot as the case may be on those parts of the tape so subdivided.

The figures shall be well raised by deep etching, and their background shall be finished dead black.

(f) *Overall length.* As required.

(g) *Calibration and Allowable Error.*

(i) When the whole length of the tape, supported throughout, is held horizontally at 20° C and under 10-lb tension, the distance between its first and last graduations shall not be in error by more than 0·1 ft per hundred feet of its length.

(ii) The tape shall be proved to meet the preceding condition either by National Physical Laboratory Certificate or by a written statement from a responsible and skilled person or firm that the tape has been efficiently compared with a standard tape carrying N.P.L. Certificate, the statement also setting out the error determined by this comparison.

(h) *Emblem or name.* This shall include the lettering "I.P. No. X," in which X is the Institute of Petroleum Specification Number or Reference; and such other markings as desired.

2. *Spring Balance.*

(a) *Material.* Brass body and handle, nickel-plated, with steel spring and hook.

(b) *Construction.* The balance shall be of the usual design and shall have a loop handle at one end, through which to apply tension, and at the other a hook for attaching it to the tape swivel, this hook to be fitted with a self-

closing device, so that the tape does not become detached if tension is slackened.

(c) *Graduation.* The balance shall be graduated to show every $\frac{1}{4}$ lb from 0 to 20 lb. The smaller scale divisions shall not be less than $\frac{1}{32}$ in apart and the 10-lb mark shall be clearly indicated.

(d) *Calibration and Allowable Error.* When a weight of 10 lb is hung on the hook of the balance, the reading of the pointer on the scale shall not be in error by more than $\frac{1}{4}$ lb.

3. *Step-Over.*

(a) *Construction.* The step-over is a frame holding two scribing points rigidly and at such a distance apart as meets the conditions of use laid down in the Strapping Method, Section 2 (*j*). The frame may be constructed of any material that secures this; if made of wood, it should be painted if there is any risk of its getting wet in use. Suitable designs are illustrated in Appendix I.

B. *Internal Measurement Method.*

1. *Internal Measurement Tapes.*

(a) *Material.* Carbon steel of the best quality, as currently used for measuring tapes.

(b) *Construction.* Each tape shall be fitted with a D-loop at its end allowing easy attachment of the dynamometer. Tape reels, cases, and any other incidental fittings not specifically mentioned in this specification may be ordered as desired.

(c) *Dimensions.* Width $\frac{3}{8}$ in; thickness approximately 0·01 in.

(d) *Graduation.*

(i) Graduation shall be on one side only of the tape.

(ii) The zero graduation shall be at the outside of the end of the D-loop (" D-loop included ").

(iii) The tape shall be graduated at every whole foot of its length from its zero, and

(iv) All or any part of it may be further divided into inches and tenths of inches as desired.

(e) *Figuring.* The length from the zero graduation shall be clearly shown at every whole foot, with figuring at every inch on those parts of the tape so divided.

The figures shall be well raised by deep etching, and their background shall be finished dead black.

(f) *Overall length.* As required.

(g) *Calibration and Allowable Error.*

(i) When the whole length of the tape, supported throughout, is held horizontally at 20° C and under 10-lb tension the distance between its first and last graduations shall not be in error by more than 0·01 ft per hundred feet of its length.

(ii) The tape shall be proved to meet the preceding condition either by National Physical Laboratory Certificate or by a written statement from a responsible and skilled person or firm that the tape has been efficiently compared with a standard tape carrying N.P.L. Certificate, the statement also setting out the error determined by this comparison.

(iii) The weight of the tape in lb per foot shall be certified by the manufacturers, or determined satisfactorily otherwise.

(h) *Emblem or Name.* This shall include the lettering "I.P. No. X," in which X is the Institute of Petroleum Specification Number or Reference; and such other markings as desired.

2. *Redwood Dynamometer.*

(a) *Material.* Brass body, wooden handle, dry cell battery receptacle, electric buzzer, with steel spring and hook.

(b) *Construction.* This shall be of the general construction shown in Appendix II, consisting essentially of a spring balance so fitted with electric contacts that at a pull of 10 lb on the hook of the balance, a buzzer sounds.

(c) *Graduation.* The balance shall be graduated to show every $\frac{1}{4}$ lb from 0 to 20 lb. The smallest scale division shall not be less than $\frac{1}{32}$ in apart.

(d) *Calibration and Allowable Error.* When the appropriate weights are hung on the hook of the dynamometer, the electrical contact shall preferably operate the buzzer at 10-lb pull, and in any case not below $9\frac{3}{4}$-lb or above $10\frac{1}{4}$-lb pull.

(e) *Emblem or Name.* This shall include the lettering "I.P. No. X," in which X is the Institute of Petroleum Specification Number or Reference and "REDWOOD DYNAMOMETER."

3. *Scale or Rule.*

(a) *Materials.* Boxwood or lancewood; and brass.

(b) *Construction.* The rule shall be of the type with brass-tipped ends, commonly used by drapers.

(c) *Dimensions.* The rule shall be 3 ft in length, 1 in wide, and $\frac{3}{16}$ in thick.

(d) *Graduation.* This to be feet, inches, and tenths of an inch throughout.

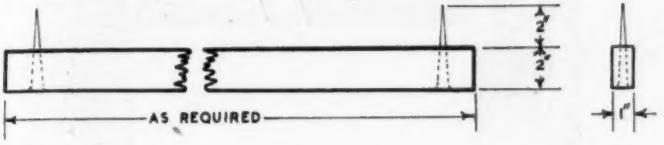
(e) *Calibration.* The rule shall bear the acceptance stamp of the Board of Trade.

APPENDIX I.

STEP-OVERS.

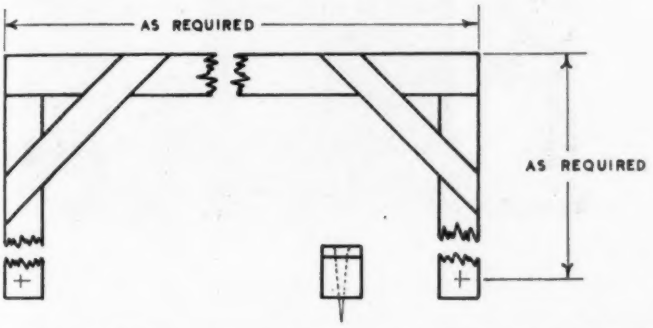
For small obstructions.

Two long nails, their points sharpened for scribing, are driven through, say, 2-in by 1-in wood batten.



For large obstructions.

A U-frame, say, of 2-in by $\frac{1}{4}$-in wood, with thicker pieces firmly nailed on at its points, has two similar nails driven through these last.



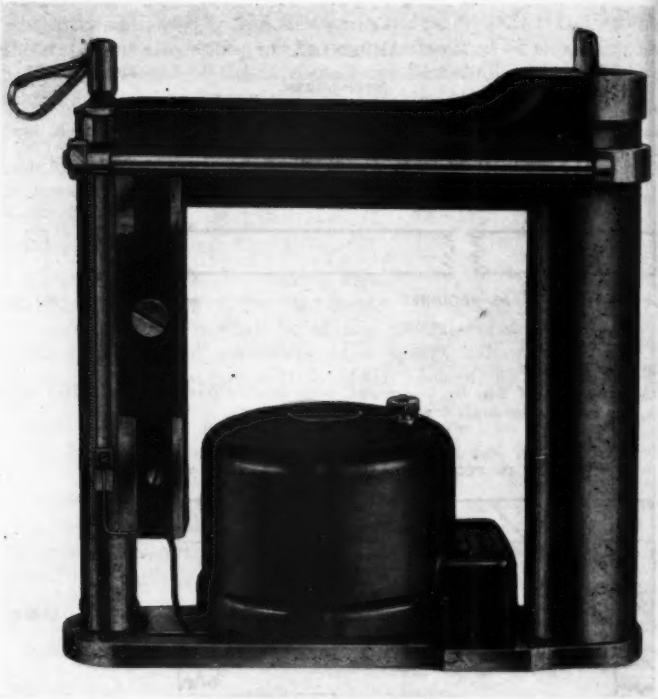
The frame is best designed to pass under or above the obstruction, not in front of it.

In both cases.

Rigid construction is essential.

The wood should not warp, and the frame should be painted if there is risk of its getting wet in use.

APPENDIX II.



REDWOOD DYNAMOMETER.